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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS,
ERNEST MERRITT, and FREDERICK BEDELL

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AUGUST, 1911

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THE

PHYSICAL REVIEW.

A VERIFICATION OF THE THEORY OF BROWNIAN MOVEMENTS AND A DIRECT DETERMINATION OF THE VALUE OF *NE* FOR GASEOUS IONIZATION.[1]

By Harvey Fletcher.

Introduction.

In 1827 a botanist named Brown noticed that small particles which were suspended in a liquid were in a continual state of agitation; but it was not until 1889 that the correct explanation of this phenomenon was given, when Gouy[2] suggested that it was due to molecular bombardments. In 1905 Einstein[3] deduced a formula which makes it possible to calculate the magnitude of the Brownian displacements. Perrin,[4] Henri,[5] Chandesaignes,[6] and others, working with minute particles suspended in a liquid, obtained results which gave a fair agreement between the calculated and observed values of the displacement. Broglie,[7] who worked with particles of tobacco smoke suspended in air at atmospheric pressure, obtained displacements of the same order of magnitude as given by Einstein's formula.

In the first part of this paper a modification of this formula is proposed, and a new method is given for studying Brownian movements. Formulæ are deduced which give the probable distribution of a great many observed values of:

(1) The displacement of a particle due to Brownian movements.

[1] A brief summary of this paper was given in Science, February 17, 1911, and a more complete abstract in Phys. Zeit., 12, 1911, pp. 202–208.

[2] Journ. de Phys., T. 7, 1888, p. 561.

[3] Ann. de Phys., 4″ Series, T. XVII., p. 549, 1905.

[4] Le Radium, T. 6, p. 353, December, 1909.

[5] Compt. Rend., T. 146, 1908, p. 1024, and T. 147, p. 65, 1908.

[6] Compt. Rend., T. 147, 1908, p. 1024.

[7] Le Radium, T. 6, p. 203, July, 1909.

(2) The actual displacement in a given time of a particle acted on by a constant force.

(3) The actual time of fall through a fixed distance of a particle acted on by a constant force.

In the second part experimental results are given which verify the equations of Part I., and which make it possible to determine directly the value of Ne for gaseous ionization.

Part I. Theoretical Considerations.

§ 1. *Distribution of the displacements in successive equal intervals of time of a small spherical particle which is under the influence of no outside forces except the impacts of the gas molecules.*

Since the momentum imparted to the particle by the gas molecules is different in different directions, and changes with the time, the displacement in a given time will continually change its direction and magnitude. To find the chance that a displacement between x and $x+dx$ will occur in a time t, let us use an analysis similar to that which was first used by Maxwell to determine the distribution of molecular velocities.

Let $f(x, y, z)dxdydz$ be a function which gives the chance that a displacement lies between (x, y, z) and $(x+dx, y+dy, z+dz)$. As this chance must be the same in all directions, $f(x, y, z)$ must be invariant under a transformation of axes. By a well-known theorem of invariants, we know that the only function satisfying this condition is $f(x^2+y^2+z^2)$, *i. e.*, a function of the radius vector.

If $F(x)dx$ is the chance that the x component of the displacement is between x and $x+dx$, then the chance that the y component is between y and $y+dy$, and that the z component is between z and $z+dz$, is $F(y)dy$ and $F(z)dz$, respectively. Then, assuming[1] that the x component of the displacement is independent of y and z, we have

$$f(x, y, z)dxdydz = f(x^2+y^2+z^2)dxdydz = F(x)dx \cdot F(y)dy \cdot F(z)dz.$$

Solving,

$$f(x^2) = A^2F(x),\ f(y^2) = A^2F(y),\ f(z^2) = A^2F(z),$$

where

$$A = F(0).$$

Then

$$f(x^2+y^2+z^2) = \frac{1}{A^6} f(x^2) \cdot f(y^2) \cdot f(z^2).$$

Substitute

$$\log \left\{ \frac{1}{A^3} f(x^2) \right\} = H(x^2).$$

[1] Boltzman objected to a similar assumption in Maxwell's work, but obtained the same formula by a more rigorous analysis.

Then $$H(x^2+y^2)=H(x^2)+H(y^2).$$

Therefore

$$H(x^2)=-\alpha x^2$$

and

$$H(y^2)=-\alpha y^2$$

and our required solution is

(1) $$f(x, y, z)=A^3e^{-\alpha(x^2+y^2+z^2)}.$$

Also

(2) $$F(x)dx=Ae^{-\alpha x^2}dx, \quad F(y)dyAe^{-\alpha y^2}dy, \quad F(z)dz=Ae^{-\alpha z^2}dz.$$

As (2) gives the probability that a displacement lies between x and $x+dx$, then, if η displacements of a single particle are observed, the number which will probably lie between x_1 and x_2 is given by

(3) $$n=\eta\int_{x_1}^{x_2}Ae^{-\alpha x^2}dx.$$

A and α are functions which are independent of x, and are determined by the equations:

$$\eta=\eta A\int_{-\infty}^{\infty}e^{-\alpha x^2}dx=A\eta\sqrt{\frac{\pi}{\alpha}}$$

and

$$(x^2)_a{}^*=A\int_{-\infty}^{\infty}x^2e^{-\alpha x^2}dx=A\tfrac{1}{2}\alpha^{-\frac{3}{2}}\sqrt{\pi},$$

which give

(4) $$A=\sqrt{\frac{\alpha}{\pi}},$$

(5) $$\alpha=\frac{1}{2(x^2)_a}.$$

It is plain that we can interpret η in the above formula as referring to η similar particles having displacements in one and the same interval of time t, and the same analysis will hold. With such an interpretation $(x^2)_a$ is a group average, that is to say, all the particles having displacements between o and Δx are taken in one group: those between Δx and $2\Delta x$ in a second group, and so on. It seems reasonable to suppose that the average square of the displacement during a time t of η similar particles obtained in this way is the same as the average square of the displacement of one single particle during η successive intervals of time t, and this supposition will be made in what follows.

The average displacement along any axis is zero, but the average

* In this work the subscript a has been used to denote an average value, and the subscript p to denote the most probable value.

absolute value of the displacement, that is, the average of the positive or negative displacements is

$$x_a = 2\sqrt{\frac{\alpha}{\pi}}\int_0^\infty xe^{-\alpha x^2}dx = \sqrt{\frac{2}{\pi}}\sqrt{(x^2)_a}. \tag{6}$$

In order to find the absolute displacement in space, change $f(x, y, z)$ in (1) to spherical coördinates by the transformations

$$r^2 = x^2+y^2+z^2; \quad x = r\cos\theta; \quad y = r\sin\theta\cos\varphi; \quad z = r\sin\theta\sin\varphi.$$

Then the number out of η displacements that lie between r and $r+dr$ is

$$dn = \eta\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} r^2e^{-\alpha r^2}dr\int_0^{2\pi} d\varphi\int_0^{\pi}\sin\theta d\theta,$$

or

$$dn = \eta 4\pi\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} r^2e^{-\alpha r^2}dr. \tag{7}$$

This function has a maximum at $\alpha r^2 = 1$. Therefore the most probable displacement is given by

$$r_p = \sqrt{2}\sqrt{(x^2)_a}. \tag{8}$$

The average displacement in space is

$$r_a = 4\pi\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\int_0^\infty rr^2e^{-\alpha r^2}dr = 2\sqrt{\frac{2}{\pi}}\sqrt{(x^2)_a}. \tag{9}$$

which shows that $r_a = 2x_a$.

It is also useful for comparison with observation to find an expression for the average displacement in a plane. The chance that the projection of the displacement on the xy plane is between (x, y) and $(x+dx, y+dy)$ is $F(x)dx\cdot F(y)dy$, or

$$\frac{\alpha}{\pi}e^{-\alpha(x^2+y^2)}dxdy.$$

Now transform by the relations

$$x = R\cos\theta \text{ and } y = R\sin\theta,$$

and we get for the number out of η displacements that lie between R and $R+dR$

$$dn = \eta\frac{\alpha}{\pi}Re^{-\alpha R^2}dR\int_0^{2\pi} d\theta,$$

or

$$dn = 2\eta\alpha Re^{-\alpha R^2}dR. \tag{10}$$

This shows a maximum at $\alpha R^2 = \frac{1}{2}$, or the most probable value of the displacements in a plane is

$$R_p = \sqrt{(x^2)_a}. \tag{11}$$

The average projection of the displacement on a plane is

$$R_a = 2\alpha \int_0^\infty R^2 e^{-\alpha R^2} dR = \sqrt{\frac{\pi}{2}(x^2)_a}. \tag{12}$$

So we see that if the value of $(x^2)_a$ can be determined, the distribution of the displacements, the average and most probable values of the displacements along an axis, in a plane, or in space can be calculated.

§ 2. *Resistance offered by a gaseous medium to a spherical particle moving uniformly through it.*

Before obtaining an expression for $(x^2)_a$ from dynamical considerations, it is necessary to consider the law of motion of a small particle moving through the gas. Stokes gave an approximate solution to this problem by starting from the fundamental equations of hydrodynamics. However, in solving, it was necessary to make the following assumptions and approximations.

1. A continuous medium.
2. An incompressible fluid.
3. Uniform density.
4. No impressed force upon the gas.
5. The mathematical approximation that the square of the velocity of the gas at any point is negligible.
6. No slip at the surface of the particle.

If F is the force acting upon a particle of radius a, moving with a constant velocity v, through a gas whose coefficient of viscosity is μ, then, with the above assumptions,

$$F = 6\pi\mu a v. \tag{13}$$

If we assume that there is external friction at the surface of the particle, the hydrodynamical[1] equations show that

$$F = 6\pi\mu a k' v, \tag{14}$$

where

$$k' = \frac{1 + \frac{2\mu}{\beta a}}{1 + \frac{3\mu}{\beta a}}, \tag{15}$$

β being the coefficient of external friction. Or, if the coefficient of slip, defined by the equation

$$\rho = \frac{\mu}{\beta}$$

[1] Bassett's Hydrodynamics.

be introduced,

$$k' = \frac{1 + 2\frac{\rho}{a}}{1 + 3\frac{\rho}{a}},$$

and if we can neglect $(\rho/a)^2$ in comparison to ρ/a,

$$k' = \frac{1}{1 + \frac{\rho}{a}}. \tag{16}$$

In order to take account of the molecular structure of the gas, Cunningham[1] has modified Stokes's formula by considering the impacts of the gas molecules upon the particle and has deduced from the theory of probability that

$$F = 6\pi\mu akv, \tag{17}$$

where[2]

$$k = \left(1 + \frac{\frac{3}{2}\frac{l}{a}}{f - 2(f-1)}\right)^{-1}, \tag{18}$$

l being the mean free path of the gas molecule, and f the fraction of the total number of impacts which are elastic. Experiments[3] on oil drops suspended in air at atmospheric pressure show that, at least for the range investigated, if f is put equal to zero, this formula agrees fairly well with the experimental results. Then (18) reduces to

$$k = \frac{1}{1 + \frac{3}{4}\frac{l}{a}}. \tag{19}$$

It is seen that these two formulæ become the same if we place

$$\rho = \tfrac{3}{4}l.$$

From considerations of the kinetic theory, Meyer[4] has deduced the formula for the coefficient of slip

$$\rho = \frac{4}{B}\,0.3097l,$$

where B is a number between 0 and 2 depending upon the loss of velocity

[1] Proc. Roy. Soc., Vol. A 83, No. A 563, 1910, page 357.
[2] See note 3, page 380, Phys. Rev., April, 1911.
[3] Millikan, Phys. Rev., April, 1911.
[4] Meyer, Die Kinetische Theorie der Gase, p. 211.

of the molecule upon hitting the surface of the particle. Maxwell[1] gives for the inelastic case

$$\rho = \tfrac{2}{3}l.$$

So we see that either Basset's hydrodynamical formula or Cunningham's probability formula is sufficient to represent the experimental facts as long as l/a is small compared to 1. But when l/a becomes greater than 1, they are very different, for in the former k always lies between 1 and $\frac{2}{3}$, while in the latter, k lies between 1 and 0.

In either case, if m is the mass of the particle, then its velocity of steady fall is

$$v = \frac{mg}{6\pi\mu ak}.$$

§ 3. *The average square of the displacement due to molecular impacts.*

If X is the x component of the forces due to the unbalanced molecular impacts of the gas molecules, then the equation of motion along the x axis is

$$m\frac{d^2x}{dt^2} = -F + X,$$

or

$$m\frac{d^2x}{dt^2} = -6\pi\mu ak\frac{dx}{dt} + X. \tag{21}$$

Multiply by x and substitute $d(x^2)/dt = z$, and $dx/dt = v$ and we get

$$\frac{m}{2}\frac{dz}{dt} + 3\pi\mu akz = mv^2 + Xx.$$

If η similar equations are written representing the motion at the same instant of time of η similar particles, then grouped and averaged as indicated in § 1 there results

$$\frac{m}{2}\frac{dz_a}{dt} + 3\pi\mu akz_a = \frac{m}{\eta}\sum_1^{\eta} v_n^2 + \frac{1}{\eta}\sum_1^{\eta} X_n x_n.$$

It is obvious that when η is very large

$$\Sigma Xx = 0,$$

as then there would be a group of particles having a negative $X_n x_n$ for every one having a positive $X_n x_n$. Also, since the average kinetic energy of a single particle taken over a long period of time may be taken to be the same as the average kinetic energy of a great many similar particles at any instant of time, $\frac{1}{2}\frac{m}{\eta}\sum_1^{\eta} v_n^2$ is equal to the average energy of

[1] Maxwell's Scientific Papers, Vol. II., p. 709.

translation in the direction of x of any one of the particles during a long interval of time. If ϵ is the average energy of agitation of the gas molecule and we assume that, on the average, this energy is distributed equally among three rectangular components; then, according to the law of equal partition of energy,

$$\frac{1}{2}\frac{m}{\eta}\sum_{1}^{n} v_n^2 = \frac{1}{3}\epsilon. \tag{22}$$

With these assumptions (21) reduces to

$$\frac{m}{2}\frac{dz_a}{dt} + 3\pi\mu a k z_a = \frac{2}{3}\epsilon,$$

the solution of which is

$$z_a = \frac{2}{3}\epsilon\frac{1}{3\pi\mu a k} + Ae^{-\frac{6\pi\mu a k t}{m}}.$$

The last term is negligible for any time large enough to measure. Therefore,

$$(x^2)_a = \frac{2\epsilon t}{9\pi\mu a k}, \tag{23}[1]$$

where the displacement is measured from the origin.

It is plain from the manner in which the formula for $(x^2)_a$ was derived that it represents the average square of the displacement along the x axis during a time t of a larger number of similar particles, which is taken as the same as the average square of the displacement of a single particle during a larger number of successive equal intervals of time t.

Since $\sum Xx$ necessarily oscillates about zero as n increases it will not only be negligible for n infinite but for many finite values of n and for each of these a solution similar to (23) would be obtained, but the coefficient of t, in general, would be different. Physically, this only means that the average of one series of displacements would not be exactly the same as that of another unless the two series contain an infinite number of displacements.

If the value of $(x^2)_a$ is placed in the formula deduced in § 1, we have the following six forms giving the magnitude of the Brownian displacement.

$$\sqrt{(x^2)_a} = \sqrt{2}K, \tag{23'}$$

$$r_a = \frac{4}{\sqrt{\pi}}K, \tag{9'}$$

[1] This formula was first deduced by Einstein (Ann. d. Phys., 17, p. 559, 1905) and given in essentially the same form as above by Langevin (Compt. Rend., 146, 1908, p. 530). The factor k was not in their formulæ.

(6′) $x_a = \frac{2}{\sqrt{\pi}} K,$ (11′) $R_p = \sqrt{2}K,$

(8′) $r_p = 2K,$ (12′) $R_a = \sqrt{\pi}K,$

where

$$K^2 = \frac{\epsilon t}{9\pi\mu a k}.$$

§ 4. *Effect of Brownian movements upon a small spherical particle moving under the influence of a constant outside force.*

Let the actual displacement be divided into two parts, that due to gravity, and that due to the Brownian movements. The former is simply Vt, where V is a constant, and t is the displacement in one second or the velocity due to gravity. The latter on the average is proportional to the square root of t [see (23)]. In order to treat the problem mathematically it will be assumed that each single displacement due to the Brownian movements may be represented by (24)

(24) $$x = u\sqrt{t},$$

u, the displacement in one second due to the Brownian movements, being independent of the time, and varying in different observed values of the displacement in such a way as to give x a distribution represented by (3). This assumption, which amounts to replacing the perfectly disorganized system by a more regular system which has the same distribution and average value of the displacement, seems reasonable, and the results to which it leads may be checked by experiment.

If the value of x from (24) and the value of α from (5) and (23) is substituted in (3), we obtain an expression for the distribution of the values of u, namely

(25) $$u = \eta \sqrt{\frac{h}{\pi}} \int_{u_1}^{u_2} e^{-hu^2} du,$$

where

(26) $$h = \frac{9\pi\mu a k}{4\epsilon}.$$

The average value of u is given by

$$u_a = 2\sqrt{\frac{h}{\pi}} \int_1^\infty u e^{-hu^2} du = \sqrt{\frac{1}{\pi h}},$$

or

(27) $$u_a = 3\sqrt{\pi}\sqrt{\frac{\epsilon}{\pi\mu a k}},$$

which is the same as (6) for $t = 1$, as it should be. Then, if the total displacement is designated by b, we have

$$b = Vt + u\sqrt{t}. \tag{28}$$

To obtain an expression for the distribution of the total displacements in a fixed time, we treat V and t in (28) as constants and by means of this equation change the variable in (25) from u to b. We get for the number out of η displacements that lie between b_1 and b_2

$$n = \eta \sqrt{\frac{h}{\pi t}} \int_{b_1}^{b_2} e^{-\frac{h}{t}(b-Vt)^2} db, \tag{29}$$

$$b_a = \sqrt{\frac{h}{\pi t}} \int_{-\infty}^{\infty} b e^{-\frac{h}{t}(b-Vt)^2} db = Vt. \tag{30}$$

This last result could have been obtained directly from (28), since t is constant and the average value of u is zero.

Similarly, to obtain an expression for the distribution of the times of fall through a fixed distance, we treat V and b as constants and change the variable from u to t and obtain for the number of times of fall which lie between t_1 and t_2

$$n = -\eta \sqrt{\frac{h}{\pi}} \int_{t_1}^{t_2} \frac{bt^{-\frac{3}{2}} + Vt^{-\frac{1}{2}}}{2} e^{-\frac{h}{t}(b-Vt)^2} dt,$$

or, putting $t_g = b/V$ and reversing the limits,

$$n = \frac{\eta V}{2} \sqrt{\frac{h}{\pi}} \int_{t_2}^{t_1} (t_g t^{-\frac{3}{2}} + t^{-\frac{1}{2}}) e^{-\frac{h}{t}(b-Vt)^2} dt. \tag{31}$$

Solving (28) for $\sqrt{t}$ we get

$$\sqrt{t} = \frac{-u + \sqrt{u^2 + 4bV}}{2V},$$

which shows that the limits corresponding to
$u_1 = -\infty$ and $u_2 = \infty$ are $t_1 = \infty$ and $t_2 = 0$ respectively.
Therefore,

$$1 = \tfrac{1}{2} V \sqrt{\frac{h}{\pi}} \int_0^{\infty} (t_g t^{-\frac{3}{2}} + t^{-\frac{1}{2}}) e^{-\frac{h}{t}(b-Vt)} dt,$$

and

$$t_a = \tfrac{1}{2} V \sqrt{\frac{h}{\pi}} \int_0^{\infty} t(t_g t^{-\frac{3}{2}} + t^{-\frac{1}{2}}) e^{-\frac{h}{t}(b+Vt)} dt = \sqrt{\frac{h}{\pi}} \int_{-\infty}^{\infty} t e^{-hu^2} du,$$

or, substituting the value of t in terms of u,

$$t_a = \sqrt{\frac{h}{\pi}} \int_{-\infty}^{\infty} \frac{2u^2 + 4bV - 2u\sqrt{u^2 + 4bV}}{4V^2} \cdot e^{-hu^2} du,$$

which gives

$$t_a = \frac{1}{4hV^2} + \frac{b}{V}, \tag{32}$$

or, solving for V,

$$V = \frac{b}{t_a}\left(\frac{1}{2} + \frac{1}{2}\sqrt{1 + \frac{t_a}{hb^1}}\right) \mp V_a\left(1 + \frac{t_a}{4hb^2}\right), \tag{33}$$

$$t_g = t_a\left(\frac{1}{2} + \frac{1}{2}\sqrt{1 + \frac{t_a}{hb^2}}\right)^{-1} \mp t_a\left(1 - \frac{t_a}{4hb^2}\right). \tag{34}$$

These formulæ show that, although the average of a great many observed distances of fall during a fixed time is the actual displacement due to gravity, the average of a great many times of fall through a fixed distance is somewhat different from the time of fall due to gravity. The difference, if small, is inversely proportional to the square of the fixed distance.

The value of the integral in (31) may be obtained by graphical means, or preferably from an error function table, since

$$\eta\sqrt{\frac{h}{\pi}} \int_{t_2}^{t_1} \frac{V}{2}(t_g t^{-\frac{1}{2}} + t^{-\frac{1}{2}})\, e^{-\frac{h}{t}(b - Vt)^2} dt = \eta \frac{1}{\sqrt{\pi}} \int_{s_1}^{s_2} e^{-s^2} ds,$$

where

$$s = \sqrt{h}\,\frac{b - Vt}{\sqrt{t}}.$$

All of the equations in this section can be applied to a particle under the influence of constant forces other than gravity, as for example, a charged particle in a uniform electric field. In this paper V', t', t_a', t_b', etc., will be used in place of the letters given above when they refer to a particle charged with a single elementary charge under the combined influence of gravity and a uniform electric field. Similarly, V'', t'', and V''', t''', etc., will refer to a particle charged with 2, 3, etc., elementary charges.

§ 5. *Effect of Brownian movements upon the apparent value of the electric charge carried by a particle suspended in a gas.*

The method of measuring e which was originated by Professor Millikan[1] consists in getting an isolated charged particle between two condenser plates and observing its velocity V_1 under the influence of gravity, and

[1] Phil. Mag., February, 1909; Science, p. 436, September 30, 1910; Phys. Zeit., No. 24, December, 1910.

then its velocity V_1' when the electric field is on. If E is the strength of the electric field in absolute electrostatic units acting upon the particle of apparent mass m' and density σ; g, the gravitational constant; and ρ, the density of the gas, then the following three equations enable one to express the value of e, the electric charge carried by the particle in terms of measurable quantities.

$$\frac{Ee + m'g}{m'g} = \frac{V_1'}{V}, \tag{35}$$

$$6\pi\mu akV_1 = m'g, \tag{20'}$$

$$m' = \tfrac{4}{3}\pi(\sigma - \rho)a^3. \tag{36}$$

Eliminating m' and a and solving for e we get

$$e = 9\sqrt{2\pi}\sqrt{\frac{(\mu k)^3}{2(\sigma - \rho)}} \cdot \frac{V^{\frac{3}{2}}(V^1 - V_1')}{E}. \tag{37}$$

(35) and (20') are derived on the assumption that Ee and $m'g$ are the only forces acting upon the drop, in other words, that the X spoken of in § 3 is zero. This is never strictly true, and therefore the observed velocities are variables, even for a particle which does not change its size, shape or the electric charge which it carries. However, (31) shows that the successive times of fall through a distance greater than 1 cm. of a particle having a radius larger than 100×10^{-6} cm., suspended in air at atmospheric pressure, differ from t_g by less than one tenth of a second. In any case, if V and V' are substituted in place of the observed velocities V_1 and V_1', the value of e should be correct and invariable.

PART II. EXPERIMENTAL APPLICATIONS.

§ 1. *Description of apparatus and method of observation.*

The apparatus which was used in these experiments was designed by Professor Millikan and the writer for the sake of testing the laws of motion of a small drop through a gas at reduced pressures; the results of this study are to be published in another paper. As will appear later, the results herein contained are completely independent of these laws. The same condenser plates which were described by Professor Millikan[1] were placed in a brass vessel which could be made air tight. The arrangement is represented in the vertical cross section in Fig. A. D_1 and D_2 represent the condenser plates. M_1 is an electro-magnet which slides the cover F off of a small hole which is bored through the top plate. M_2 is another electro-magnet which lifts the lead screen L, thus exposing

[1] PHYS. REV., April, 1911.

the air chamber between the condenser plates to the ionizing effect of a few milligrams of radium bromide. A is an ordinary atomizer. B_1, B_2 and B_3 are ebonite bushings through the walls of the brass cylinder. P represents a pump which may be used either for exhaustion or compres-

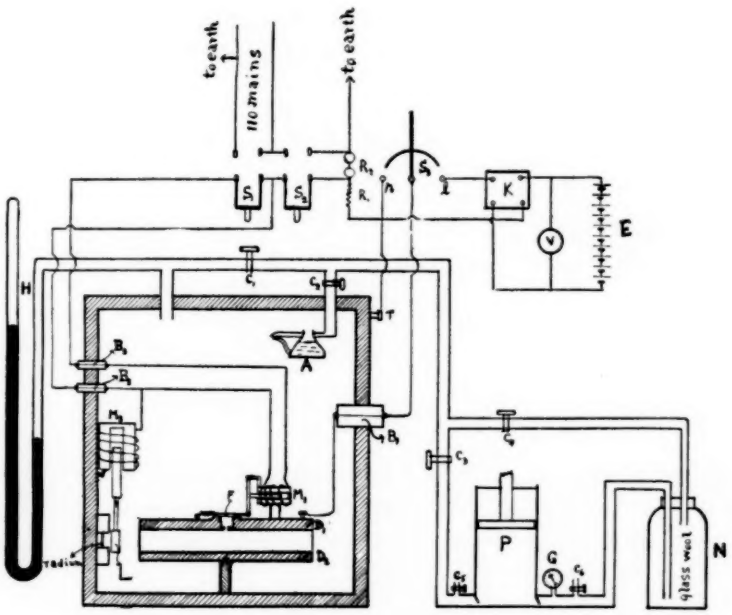

Fig. A.

sion. G is a high pressure gauge and H is a low pressure gauge or simply a U-shaped manometer. All of the air which goes into the brass vessel is made to pass through a vessel N which contains glass wool moistened with sulphuric acid. Also the interior of the large vessel is thoroughly oiled, so that the air with which the atomizer is blown and also the air contained in the vessel is dry and dust-free. C_1, C_2, C_3, C_4, C_5 and C_6 are ordinary stop cocks. The enclosing brass cylinder is connected by means of the binding post T through the resistances R_1, 20 ohms, and R_2, 450 ohms, to earth. The switch S_3, when in contact with the mercury cup r, short circuits the two plates D_1 and D_2 and connects them to earth, and when in contact with the mercury cup l, produces an electrostatic field between the plates, the intensity of which is measured by the voltmeter V. K represents a commutator. The knife edge double pole switches S_1 and S_2 operate the electro-magnets M_1 and M_2 respectively.

The horizontal cross section in Fig. B shows the method which was used to illuminate the small oil droplet. Light from an electric arc A

is made very slightly convergent by a plano-convex lens L, and then passes through a column of water 40 inches long which absorbs practically all of the radiant heat. To prevent the light from falling upon either plate it is passed through a slit s before entering the large cylinder, and then through the plane glass windows W_1 and W_4, falling upon the oil drop near the center of the plate. The illuminated oil drop is observed through the telescope T which is placed at an angle of about 172° with

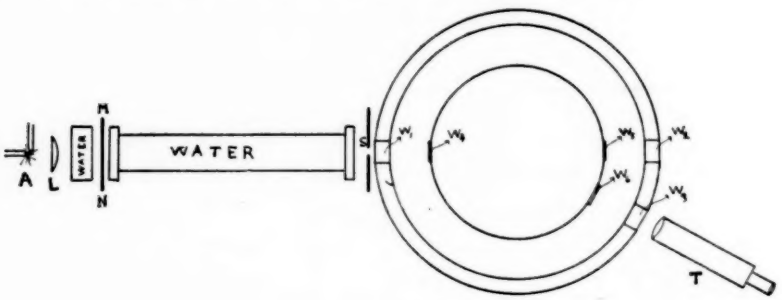

Fig. B.

the incident beam. A scale with seven large divisions subdivided into tenths is placed at the focus of the objective and viewed by the eye-piece. The screen MN serves to cut off all of the light and heat from the arc except when an observation is being taken.

To take a set of observations, C_1, C_2 and C_6 (Fig. A) are opened, and the air is exhausted from the large vessel until the manometer H shows the desired pressure. Then these stop-cocks are closed and C_4 and C_5 are opened and the air is compressed in the vessel N. The cover F is removed by closing the switch S_1; C_2 is opened, and the atomizer produces a fine oily spray which falls through the small hole in the top plate, and which finally comes between the condenser plates into the beam of light, where it can be seen by the aid of the telescope. In this spray of oil the individual drops differ very much in size and the magnitude of the charge which they carry—the smaller showing strong Brownian movements while the larger ones are almost wholly unaffected. Since they would then have different velocities both in the gravitational field and electrostatic field it is possible to select any desired droplet and keep it in the field of view; and, at the same time, rid the field of all the others.

If at any time the droplet should become uncharged and continue to fall after the electrostatic field is turned on, the lead screen L is lifted by closing the switch S_2, thus permitting the radium to produce ions in the space between D_1 and D_2, some of which are soon caught by the droplet. By adjusting the strength of the field, the droplet may be

balanced, or made to move up or down with any speed that is desired. In this way small drops which have shown strong Brownian movements have been held under observation for more than five hours, in which time as high as 411 times of fall or displacements have been taken upon the same drop.

In order to calculate what the distribution of the times of fall or displacements should be, it is necessary to know the value of h. If m' is eliminated from (35) and (20′) we have

$$ak = \frac{Ee}{(V + V')6\pi\mu}, \tag{38}$$

or substituting this value in (26) and remembering that

$$\epsilon = \frac{3}{2}\frac{RT}{N},$$

there results

$$h = \frac{1}{4}\frac{Ne}{RT}\frac{E}{(V + V')}, \tag{39}$$

and

$$u_a = 2\sqrt{\frac{RT}{\pi Ne}}\sqrt{\frac{V + V'}{E}}. \tag{40}$$

This shows that *all the distributions spoken of in Part I., and also the average value of the Brownian displacement in one second can be calculated without knowing the density of the drop, the viscosity or pressure of the gas, or the law of motion of a sphere through a viscous medium. The only assumption involved is that the velocity of steady motion is proportional to the moving force*, an assumption which is fully justified experimentally both here and elsewhere. To obtain u_a and h it is only necessary to know the electrostatic field strength, the velocity of the drop in this field when it carries a single elementary charge, and its velocity when the condenser plates are short-circuited. It is very easy to tell what velocity in the electric field corresponds to a single elementary charge, as has been explained elsewhere.[1] Since Ne/RT is known very accurately, the error in the calculated values of h and u_a depends only upon the accuracy with which E and $V + V'$ can be measured. Therefore at the beginning of each set of observations 10 or 20 times of fall and times of rise through a long distance are taken, which determine V and V' very accurately. Even though V is so small as to be materially affected by the Brownian movements, V' can always be made so large that the error in the average of 10 or 20 values of $V + V'$ is small.

[1] Millikan, PHYS. REV., April, 1911. Millikan and Fletcher, Phil. Mag., July, 1911.

§ 2. *Comparison of the observed and calculated values of the Brownian displacement in a fixed time.*

To observe directly the component of the Brownian displacement along a line, the value of Xe was made equal and opposite to mg so that on the average the drop travelled neither up nor down. The vertical distance of the drop from some reference line in the eyepiece was noted every 10 seconds. Then the difference in two consecutive readings gives

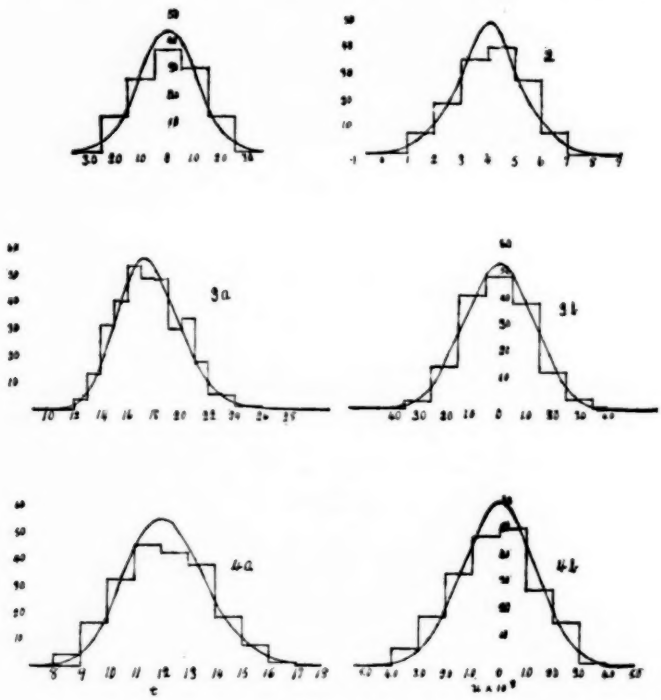

Fig. 1.

directly the Brownian displacement. Table I. shows the results obtained for a single oil drop. In the first part are the data which determine V and V'; in the second part the displacements are arranged not in the order in which they were observed but according to their magnitude. In the last part "obs n" is the number of these displacements which lie between x_1 and x_2 and "cal n" is the value of n obtained from (3). The comparison between "obs n" and "cal n" is shown graphically in curve 1 (Fig. 1). The smooth curve is obtained by plotting values of $\eta \sqrt{\frac{\pi}{\alpha}} e^{-ax^2}$ as ordinates and x as abscissas, while the broken curve is obtained from values of "obs n" in Part III. of Table I. The abscissas are expressed n terms of the eye-piece scale divisions.

TABLE I.

Drop No. 1. *Temperature* = 23° C. *Pressure* = 2.12 *cm.*

t for .522 cm.		t' for .522 cm.		
40.6	39.4	14.1	13.9	V = .01311
40.5	38.6	13.9	14.2	V' = .03725
40.3	41.0	13.6	13.9	Volts = 334.5
39.0	39.0	14.0	14.0	h = 4.05×10^4
39.2	40.7	14.4	14.2	

$x \times .00746$ cm. for 10-second intervals.

+2.39	+1.50	+ .90	+.67	+.15	−.08	−.30	−.75	−1.12	−1.80
2.09	1.50	.90	.67	.15	.15	.30	.75	1.20	1.80
2.02	1.42	.10	.60	.08	.15	.37	.75	1.20	1.87
1.87	1.35	.90	.52	.08	.15	.37	.75	1.20	1.87
1.80	1.27	.90	.52	.08	.22	.37	.82	1.22	1.87
1.74	1.27	.82	.52	.00	.22	.37	.82	1.27	1.94
1.72	1.27	.82	.52	.00	.22	.45	.82	1.27	2.09
1.65	1.20	.75	.52	.00	.22	45	.82	1.35	2.32
1.65	1.20	.75	.37	.00	.30	.52	.97	1.42	2.46
1.65	1.20	.75	.37	.00	.30	.60	.97	1.57	
1.65	1.05	.75	.37	.00	.30	.60	.97	1.57	
1.50	.97	.75	.30	.00	.30	.67	.97	1.67	
1.50	.90	.75	.15		.30	.67	.97	1.72	

obs $x_a = 8.95\times10^{-3}$ cm. cal $x_a = 8.76\times10^{-3}$.

$x_1 \times .00746$	$x_2 \times .00746$	cal n	obs n
+2.5	+1.5	9.6	13
+1.5	+0.5	29.7	31
+0.5	−0.5	43.4	38
−0.5	−1.5	29.6	27
−1.5	−2.5	9.6	13

§ 3. *Comparison of the observed and calculated values of the displacement produced in a fixed time when an outside force is acting upon the droplet.*

In this case the drop was allowed to move slowly against g and its displacement in successive 10-second intervals was taken. The results are tabulated in Table II. in a manner exactly like that used in the previous section, "cal n" being taken from (29) and u_a from (28). The graphical comparison is shown in curve 2, Fig. 1.

§ 4. *Comparison of the observed and calculated values of the time of fall through a fixed distance.*

Most of the data were taken by this method because it is capable of giving higher accuracy than that obtainable with either of the other

Table II.

Drop No. 2. Temperature = 21° C. Pressure = 2.08 cm.

t for .522 cm.		t'' for .522 cm.		
28.8	26.0	17.0	17.1	$V = .01933$
27.1	26.3	19.4	16.1	$V'' = .00303$
26.0	27.0	16.2		$V + V' = .01118$
27.5	27.6	17.5		Volts = 107.5
				$h = 5.91 \times 10^4$

$b + .00746$ for 10-second intervals.

1.4	2.5	3.0	3.4	3.8	4.2	4.5	5.0	5.2	5.7
1.5	2.5	3.1	3.4	3.8	4.2	4.5	5.0	5.2	5.9
1.5	2.5	3.1	3.4	4.0	4.2	4.5	5.0	5.3	5.9
1.7	2.6	3.1	3.5	4.0	4.3	4.6	5.0	5.3	6.1
1.8	2.7	3.1	3.5	4.0	4.3	4.6	5.0	5.3	6.2
1.9	2.8	3.2	3.6	4.0	4.3	4.6	5.0	5.4	6.2
1.9	2.8	3.2	3.6	4.0	4.3	4.6	5.1	5.4	6.2
2.0	2.8	3.2	3.6	4.0	4.4	4.7	5.1	5.4	6.3
2.1	2.9	3.2	3.7	4.1	4.4	4.7	5.2	5.4	6.4
2.1	3.0	3.2	3.7	4.2	4.5	4.7	5.2	5.5	
2.1	3.0	3.2	3.7	4.2	4.5	4.8	5.2	5.5	
2.2	3.0	3.3	3.7	4.2	4.5	4.9	5.2	5.5	
2.3	3.0	3.3	3.8	4.2	4.5	4.9	5.2	5.5	
2.5	3.0	3.3	3.8	4.2	4.5	5.0	5.2	5.5	

obs $u_a = 2.365 \times 10^{-3}$. cal $u_a = 2.32 \times 10^{-3}$.

$b_1 \div .00746$	$b_2 \div .00746$	cal n	obs n
$-\infty$	0	.00	0.0
0	1	.88	0.0
1	2	5.56	7.5
2	3	20.04	18.5
3	4	38.80	35.0
4	5	39.40	39.5
5	6	22.40	27.5
6	7	6.65	8.0
7	$+\infty$	1.32	0.0

methods. In all of the observations recorded in this section, except those relating to Drop No. 8, the variation in the time of fall was taken under the influence of gravity alone. But since (21) shows that V is proportional to $1/ak$ while u_a is proportional to $1/V\overline{ak}$ the Brownian movements would affect the velocity less at a low pressure than at a high pressure. In order to work, however, at a low pressure where the Brownian movements are large, for Drop No. 8 the velocity was made small by superposing an electric field upon the gravitational field. However there is an objection to this procedure since a very slight change in the strength

of the electrostatic field produces a very perceptible change in the velocity of the drop.

The results are tabulated in a manner similar to that used in sections 2 and 3. For example in Table III., Part I., in the column "t'" are given values of the time in seconds required for the singly charged drop to move .522 cm. under the influence of the electrostatic field; and simi-

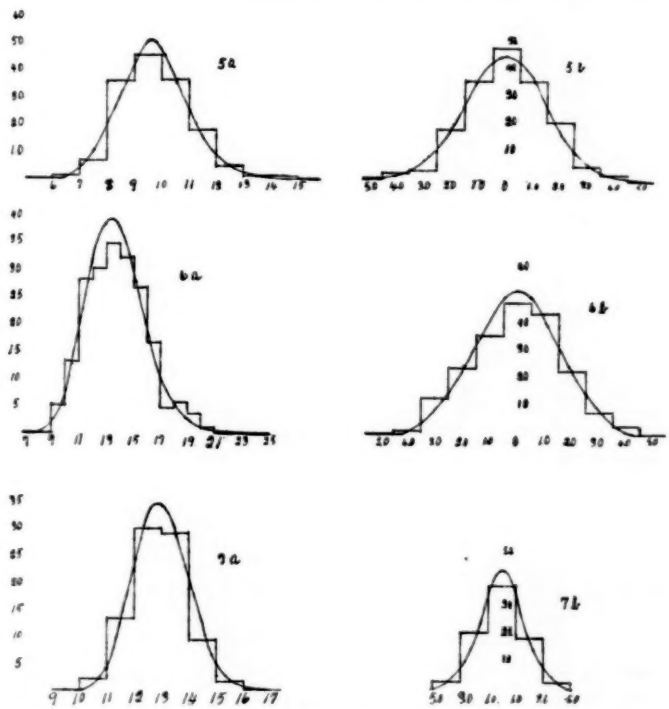

Fig. 2.

larly in the columns, t'', t''' and t^{iv} are given the values of the time for the same drop when it is charged with two, three and four elementary charges. It is seen from the values in the last column that

$$V + V' = \tfrac{1}{2}(V + V'') = \tfrac{1}{3}(V + V''') = \tfrac{1}{4}(V + V^{iv}),$$

as the theory predicts. Therefore the values $\frac{1}{2}(V+V'')$, $\frac{1}{3}(V+V''')$ and $\frac{1}{4}(V+V^{iv})$ were used to determine the mean value of $V+V'$. Also in the last column is given the value of h computed from (39). In part II. are given the successive times of fall through .0373 cm. At the bottom are given the average values obtained from these times of fall. V is computed by (33) and "cal u_a" by (40). The theory predicts that the average component of the displacement in one second along a line

should be $.945\times10^{-3}$ and the displacement observed was $.990\times10^{-3}$. In Part III. is shown the comparison of the observed and calculated

TABLE III.

Drop No. 3. Temperature = 20° C. *Pressure* = 23.1 *cm.*

Part I.		b = .522 cm.		Volts = 637.
t'	t''	t'''	t^{iv}	
58.0	26.0	16.3	11.6	V = .00213
59.0	25.5	16.4		V' = .00881
58.2	25.7	17.0		V'' = .0205
59.5	26.3	16.5		V''' = .0315
58.4	26.0			V^{iv} = .0437
	26.4			Mean $V+V'$ = .0111
	25.9			$h = 35.6\times10^4$
	26.3			

Part II.			Values of t.			b = .0373 cm.			
12.2	14.6	15.6	16.3	17.0	17.5	18.3	19.0	20.0	21.4
12.4	14.6	15.6	16.3	17.0	17.5	18.3	19.0	20.0	21.5
12.5	14.6	15.6	16.3	17.0	17.6	18.3	19.0	20.0	21.4
13.0	14.7	15.7	16.4	17.0	17.6	18.4	19.0	20.1	21.5
13.2	14.8	15.7	16.4	17.0	17.6	18.4	19.0	20.1	21.6
13.4	14.8	15.7	16.4	17.0	17.6	18.4	19.1	20.2	21.7
13.6	14.8	15.7	16.4	17.0	17.7	18.4	19.2	20.2	21.7
13.7	14.8	15.7	16.4	17.0	17.7	18.4	19.2	20.2	21.8
13.8	14.8	15.7	16.4	17.0	17.7	18.4	19.2	20.3	22.0
13.8	14.8	15.8	16.5	17.0	17.7	18.5	19.4	20.3	22.2
13.8	14.9	15.8	16.5	17.0	17.8	18.5	19.4	20.4	22.2
13.9	14.9	15.8	16.5	17.1	17.8	18.5	19.4	20.4	22.5
14.0	14.9	15.8	16.6	17.1	17.8	18.5	19.4	20.4	22.5
14.0	15.0	15.8	16.6	17.1	17.8	18.5	19.4	20.4	22.6
14.0	15.0	16.0	16.6	17.1	17.8	18.6	19.4	20.4	23.2
14.0	15.0	16.0	16.6	17.1	17.8	18.6	19.4	20.4	23.3
14.0	15.0	16.0	16.7	17.2	17.8	18.6	19.5	20.4	23.3
14.0	15.1	16.0	16.7	17.2	17.8	18.6	19.5	20.4	23.3
14.0	15.1	16.0	16.7	17.2	18.0	18.6	19.5	20.4	23.3
14.0	15.2	16.0	16.7	17.2	18.0	18.6	19.5	20.4	24.3
14.0	15.2	16.0	16.7	17.2	18.0	18.6	19.5	20.4	25.4
14.1	15.3	16.1	16.7	17.2	18.0	18.7	19.6	20.6	26.3
14.2	15.3	16.2	16.7	17.3	18.0	18.7	19.6	20.6	20.9
14.2	15.3	16.2	16.7	17.3	18.0	18.7	19.6	20.6	21.0
14.3	15.4	16.2	16.7	17.4	18.0	18.8	19.7	20.6	21.0
14.3	15.4	16.2	16.8	17.4	18.0	18.8	19.8	20.7	21.1
14.4	15.4	16.2	16.8	17.4	18.1	18.8	19.8	20.7	21.3
14.4	15.5	16.2	16.8	17.4	16.1	18.8	19.9	20.7	21.3
14.5	15.5	16.3	16.8	17.4	18.1	18.8	19.9	20.7	
14.5	15.5	16.3	16 8	17.4	18.1	18.8	19.9	20.8	
14.5	15.5	16.3	16.9	17.5	18.2	18.8	20.0	20.8	
14.6	15.6	16.3	16.9	17.5	18.2	18.8	20.0	20.8	

$t_a = 17.65, V_a = .00211, V = .00213, \eta = 321$, obs $u_a = .990\times10^{-3}$, cal $u_a = .945\times10^{-3}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	u_1	u_2	obs n	cal n
0	12	0.0	.69	$+\infty$	+3.5	0	.5
12	13	3.5	3.3	+3.5	+2.5	5	5.3
13	14	13.0	10.9	+2.5	+1.5	31	27.1
14	15	31.0	24.2	+1.5	+0.5	74	75.3
15	16	35.0	40.8	+0.5	−0.5	98	105.0
16	17	53.0	52.4	−0.5	−1.5	78	75.3
17	18	48.5	54.7	−1.5	−2.5	27	27.1
18	19	48.0	47.7	−2.5	−3.5	7	5.3
19	20	29.5	35.6	−3.5	$-\infty$	1	.5
20	21	33.5	23.5				
21	22	12.5	13.7				
22	23	5.5	7.3				
23	24	5.0	3.6				
24	25	1.0	1.6				
25	26	1.0	.69				
26	∞	1.0	.47				

TABLE IV.

Drop No. 4. Temperature = 21° *C. Pressure* = 14.3 *cm.*

Part I.			δ = .522 cm.			Volts = 483.5.	
t			t'		t''	t'''	
							V = .00307
160	166	182.8	73.5	68.7	29.7	18.4	V' = .00742
158	187	175.2	71.0	70.2	28.5	18.9	V'' = .01754
158.9	178	164.4	72.8	67.4	29.1	18.8	V''' = .0279
167.0	175.6	178.0	71.0		29.0	t^{iv}	V^{iv} = .0387
161.5	176.4	169.2	68.0			13.5	V^{v} = .0607
166.2	168.0		70.0			t^{iv}	Mean $V+V'$ = .01041
170.0	170.0		70.4			8.6	$h = 28\times10^{4}$

l_a = 12.12, V_a = .00308, V = .00310, η = 202, obs $u_a = 1.061\times10^{-3}$, cal $u_a = 1.057\times10^{-3}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	u_1	u_2	obs n	cal n
0	8	0	0	$+\infty$	+4.0	0	.24
8	9	4.0	1.4	+4.0	+3.0	6	2.1
9	10	16.0	10.5	+3.0	+2.0	18	11.8
10	11	32.0	31.4	+2.0	+1.0	34	32.2
11	12	44.5	50.7	+1.0	0.0	48	55.5
12	13	42.0	50.7	0.0	−1.0	51	55.5
13	14	37.5	33.9	−1.0	−2.0	28	32.2
14	15	18.0	16.2	−2.0	−3.0	16	11.8
15	16	7.5	6.3	−3.0	−4.0	1	2.1
16	17	1.0	1.6	−4.0	$-\infty$	0	.24
17	18	.5	.1				

distributions of the values of t and u. Curves 3a and 3b, which are plotted as explained in section 2, show graphically this same comparison. In all of the following tables the drop no. and the curve no. correspond. Table III. is complete, but in Tables IV.–IX. the observed values of t in Part II. have been omitted.

TABLE V.

Drop No. 5. Temperature = 20° C. Pressure = 9.97 cm.

Part I.			$b = .522$ cm.			Volts = 318.	
t			t'	t''	t'''	t^{IV}	
127.2	132.2	135.5	107.8	38.0	22.7	17.8	$V = .003911$
129.7	132.2	136.1	106.1	38.2	23.2	17.0	$V' = .004790$
129.9	132.3	136.4	108.0	38.5	23.2	17.2	$V'' = .01352$
130.2	132.4	137.8	106.5	38.3	24.1	17.1	$V''' = .02222$
130.8	133.2	138.4	109.0	38.4	23.8	t^{V}	$V^{IV} = .03022$
131.4	133.7	138.8	113.0	39.4	23.9		$V^{V} = .03880$
131.4	134.2	139.5	113.0	39.6		13.3	Weighted mean $V + V'$
132.2	134.7		108.8			13.8	$= .0869$
							$h = 22.7 \times 10^4$

$t_a = 9.72$, $V_a = .00383$, $V = .00388$, $\eta = 171$, obs $u_a = 1.162 \times 10^{-3}$, cal $u_a = 1.183 \times 10^{-3}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	u_1	u_2	obs n	cal n
0	7	1.	.7	$+\infty$	+3.5	2	1.6
7	8	6.5	10.5	+3.5	+2.5	3	6.3
8	9	35.5	30.7	+2.5	+1.5	18	18.2
9	10	45.0	48.2	+1.5	+0.5	36	37.3
10	11	36.0	36.0	+0.5	−0.5	48	44.2
11	12	17.5	16.0	−0.5	−1.5	36	37.3
12	13	4.5	4.6	−1.5	−2.5	21	18.2
13	14	1.0	1.1	−2.5	−3.5	5	6.3
14	∞	1.0	0.2	−3.5	$-\infty$	2	1.6

TABLE VI.

Drop No. 6. Temperature = 20° C. Pressure = 7.0 cm.

Part I.		$b_1 = .521$ cm.		Volts = 828.	
t	t'		t''		
The value of V	24.5	25.0	11.2	$V = .00277$	
is obtained	24.6	24.7	11.5	$V' = .0210$	$h = 21.7 \times 10^4$
from data in	24.6	24.6	11.7	$V'' = .0446$	
Part II.	24.3	25.6	11.9		
	24.7	25.2	12.0	Weighted mean $V + V' = .02373$	
	24.6	24.6			

$t_a = 13.78$, $V_a = .00274$, $V = .00277$, $\eta = 200$, obs $u_a = 1.256 \times 10^{-3}$, cal $u_a = 1.215 \times 10^{-3}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	$u_1 \times 10^3$	$u_2 \times 10^3$	obs n	cal n
0	9	0	0.3	$+\infty$	+3.5	1	2.1
9	10	5	1.8	+3.5	+2.5	13	7.8
10	11	13	6.8	+2.5	+1.5	24	22.3
11	12	28	16.7	+1.5	+0.5	36	42.0
12	13	30	28.1	+0.5	−0.5	48	51.6
13	14	34.5	35.3	−0.5	−1.5	44	42.0
14	15	32.0	25.0	−1.5	−2.5	23	22.3
15	16	26.5	28.9	−2.5	−3.5	8	7.8
16	17	16.5	20.5	−3.5	$-\infty$	3	2.1
17	18	4.5	13.8				
18	19	5.5	7.2				
19	20	3.5	3.6				
20	21	1.5	1.7				
21	22	0.5	0.8				
22	∞	0.0	0.5				

TABLE VII.

Drop No. 7. Temperature = 20° *C. Pressure* = 6.5 *cm.*

Part I.			$b = .521$.		Volts = 668.
t	t'		t''	t	
Value of V	33.7	35.6	14.2		$V = .00579$.
is obtained	33.0	34.7	14.4	9.1	$V' = .01417$.
from data	32.8	33.0	14.7	9.3	$V'' = .0355$.
in Part II.	34.4	35.4			$V''' = .0566$.
	35.8	34.0		$\overline{t}$	$V^{IV} = .0755$.
	34.9				$h = 20.2 \times 10^4$
				6.9	Weighted mean $V + V' = .02024$.

$t_a = 12.89$, $V_a = .00577$, $V = .00579$, $\eta = 84$, obs $u_a = 1.278 \times 10^{-3}$, cal $u_a = 1.252 \times 10^{-3}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	u_1	u_2	obs n	cal n
0	10	0.0	0.04	$+\infty$	+5	0	.06
10	11	2.0	1.6	+5	+3	3	2.3
11	12	13.0	13.2	+3	+1	21	19.7
12	13	29.5	31.2	+1	−1	38	40.0
13	14	28.5	26.5	−1	−3	19	19.7
14	15	9.0	9.5	−3	−5	3	2.3
15	16	2.0	1.7	−5	$-\infty$	0	.06
16	∞	0.0	0.2				

Particular attention is to be called to Drop No. 8 which showed variations in the time of fall from 2 seconds to 25 seconds, the average velocity being 10 per cent. lower than the actual velocity due to the constant outside force. In this rather extreme case the observed and calculated values show a very good agreement.

TABLE VIII.

Drop No. 8. Temperature = 20° C. Pressure = 2.98 cm.

Part I.		b = .522 cm.		Volts = 162.7.
t		t''	t'''	
43.5	49.0	32.5	17.5	V = .01112
47.5	49.8	32.0	18.0	V'' = .01592
43.4	49.0	32.6	18.5	V''' = .02888
45.1	45.0	33.2	18.0	Mean $V + V'$ = .01346
45.1	47.6	33.2	18.4	$h = 7.52 \times 10^4$
47.4	47.2	33.4		
47.4	48.6	33.4		
47.4	48.4			

$t_a = 7.29$, $V_a' = .00205$, $V' = .00226$, $\eta = 411$, obs $u_a = 1.95 \times 10^{-3}$, cal $u_a = 2.05 \times 10^{-3}$.

Part III. Distribution of t'.				Distribution of u.			
t_1'	t_2'	obs n	cal n	u_1	u_2	obs n	cal n
0	2	.5	0.9	+8	+6	2	3.7
2	3	9.0	13.4	+6	+4	17	20.5
3	4	35.0	38.1	+4	+2	70	65.2
4	5	57.5	57.7	+2	0	108	115.2
5	6	55.5	60.8	0	−2	113	115.2
6	7	60.5	56.1	−2	−4	53	65.2
7	8	50.5	47.5	−4	−6	18	20.5
8	9	50.0	36.8	−6	−8	5	3.7
9	10	26.0	28.4				
10	11	15.5	21.3				
11	12	17.0	14.4				
12	13	12.5	10.7				
13	14	8.5	7.5				
14	15	4.0	5.5				
15	20	6.5	9.4				
20	∞	2.0	2.1				

TABLE IX.

Drop No. 9. Temperature = 20° C. Pressure = 2.28 cm.

Part I.			b = .521 cm.		Volts = 353.
t	t'		t''	t	
The value of	16.8	17.8	8.0	5.4	V = .00805
V is ob-	16.8	18.4	7.9	5.0	V' = .03024
tained	17.0	17.6	8.0	4.8	V'' = .0657
from data	16.8	17.0	7.8	4.8	V''' = .1042
in Part II.	16.6				$h = 409 \times 10^4$
					Weighted mean $V + V'$ = .0378

$t_a = 9.35$, $V_a = .00795$, $V = .00805$, $\eta = 85$, obs $u_a = 2.43 \times 10^{-3}$, cal $u_a = 2.38 \times 10^{-3}$.

Part III. Distribution of t.				Distribution of u.			
t_1	t_2	obs n	cal n	u_1	u_2	obs n	cal n
0	6	0	0	$+\infty$	+8	0	.9
6	7	1	.8	+8	+6	1	2.6
7	8	9	8.4	+6	+4	8	7.0
8	9	27	24.0	+4	+2	9	13.3
9	10	25	27.8	+2	0	27	18.5
10	11	16	16.8	0	−2	19	18.5
11	12	4	5.7	−2	−4	10	13.3
12	13	3	1.4	−4	−6	8	7.0
13	∞	0	0.2	−6	−8	3	2.6
				−8	$-\infty$	0	.9

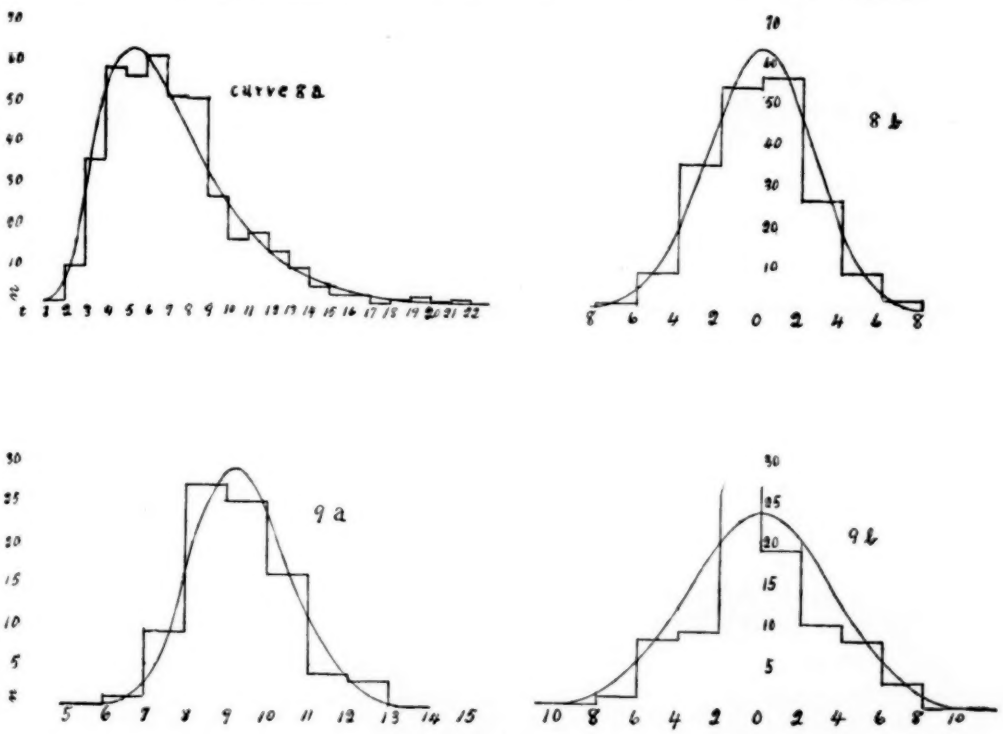

Fig. 3.

Before the condenser plates were put into the large brass cylinder described above, 341 observations were taken upon a single oil drop. 151 values of t were taken for b = .00744 cm.; 155 values for $b = 2\times$ .00744 cm.; and 34 values for $b = 5\times.00744$ cm. The comparison of the observed and calculated distributions for these three cases is shown in curves 10*a*, 10*b*, and 10*c*. The observed values of u_a were $.792\times 10^{-3}$, $.846\times10^{-3}$ and $.725\times10^{-3}$. The comparison of the observed and

calculated 341 values of u is shown in Curve 11. The two broken curves represent two different groupings of the same values of u.

Since for oil drops suspended in air at atmospheric pressure the formula

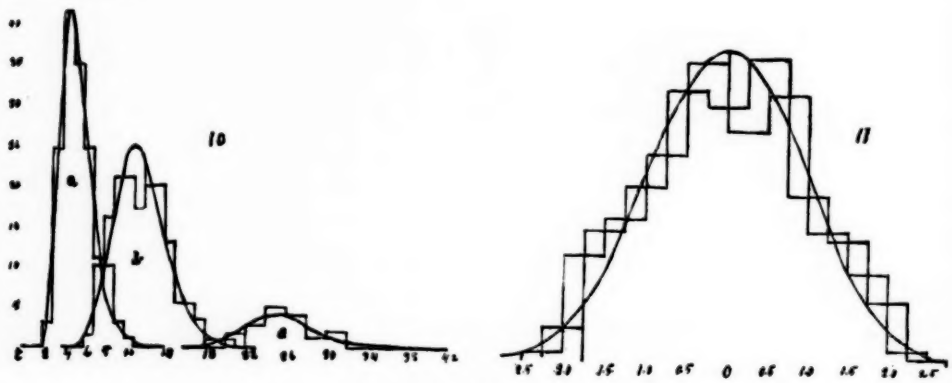

Fig. 4.

$$V = \frac{2}{9}\frac{ga^2(\sigma - e)}{\mu}\left\{1 + .817\frac{l}{a}\right\}$$

has been shown to hold it was used to determine a and k with the result that

$$a = 31.9 \times 10^{-6} \quad \text{and} \quad k = .810.$$

Substituting these values in (27) we get

$$\epsilon = 6.40 \times 10^{-14}$$

and since

$$e = \frac{3}{2}\frac{RT}{N},$$

we get ($G = 296$ and $R = 82.9 \times 10^6$)

$$N = 57.5 \times 10^{22}.$$

We see thus that the Brownian movement theory developed in Part I. accounts completely for the variation in the observed displacements and times of fall, and gives a fairly accurate means of determining molecular magnitudes.

§ 5. *Determination of the value of Ne for gaseous ionization.*

Townsend's and Frank and Westfall's work[1] on mobility and diffusion coefficients is the only evidence, so far, that has justified the assumption that the value of Ne for gaseous ionization is the same as in electrolysis.

[1] For a discussion of their results see Millikan and Fletcher, Phil. Mag., June, 1910.

The fact that the theoretical and observed distributions and the average absolute values of the displacement agree, shows that this assumption is correct. To show how close is this agreement (40) is solved for $\sqrt{Ne}$. The resulting value for each drop is given in Table X.

TABLE X.

Drop No.	$u_a \times 10^2$	T	$V+V'$	Volts.	$\sqrt{Ne} \times 10^{-7}$	η
1	2.83	294	.05036	334.5	1.68	125
2	2.365	294	.01118	107.5	1.67	136
3	.990	293	.1110	637	1.645	321
4	1.061	294	.01041	483.5	1.695	202
5	1.162	293	.00868	318	1.73	171
6	1.256	293	.0237	828	1.65	200
7	1.278	293	.0201	668	1.66	84
8	1.950	293	.133	162.7	1.785	411
9	2.43	293	.0380	353	1.65	85

If weights be assigned according to the number of observations taken as shown in the last column of the above table, there results for *the weighted mean value which represents an average of 1,735 values of u*

$$\sqrt{Ne} = 1.698 \times 10^7$$

or

$$Ne = 2.88 \times 10^{14}.$$

The value of Ne obtained by depositing silver by an electric current, when expressed in electrostatic units is 2.896×10^{14}.

If now the value of N obtained in section 4 is substituted in the above value of Ne we get[1]

$$e = 5.01 \times 10^{-10},$$

which is within 2 per cent. of the value obtained by Millikan. It is to be noticed that *both N and Ne and consequently e are determined by the above method from the same set of experiments and not from totally different types of experiments as heretofore has always been the case, and further that these experiments furnish a direct proof that the value of the elementary charge on the oil drop which it received by catching an ion from the air is the same as the charge on the silver ion in electrolysis.*

§ 6. *Application of the theory to Ehrenhaft's*[2] *and Przibram's*[3] *work on the value of e.*

[1] This shows there is no longer any discrepancy in the values of e obtained by the Millikan method and the Brownian movements method as had appeared to be the case from Perrin's observations on Brownian movements in liquids.

[2] Wien. Ber., 119, 2a, March, 1910.

[3] Wien. Ber., 119, 2a, June, 1910.

In a preliminary report of this work which was published in the Phys. Zeit., VII., 1911, I computed the distribution of the values of t and t' treating the data in Table V. of Ehrenhaft's work as if it were taken all upon one particle. Using Cunningham's formula and assuming the density of the particles to be that of metallic platinum, as Ehrenhaft supposed it to be h was calculated from (26) and found to be given by

$$h = 4.55 \times 10^{4}.^{1}$$

When, however, h is computed from (39), $V+V'$ being computed the values $t_a = 6.86$ and $t_a' = 4.18$, we have

$$h = 23.6 \times 10^{4}.$$

This very great discrepancy can, in my judgment, be explained only by assuming that the density of the particles which he observed was not the density of the metallic platinum. For other reasons Regener[2] has come just recently to the same conclusion.

Using this last value of h we get from (26)

$$ak = 11.44 \times 10^{-6},$$

and from (19)

$$a = 16.56 \times 10^{-6},$$

and from (20)

$$\sigma = 3.3.$$

From this it appears that the density of the platinum particles which Ehrenhaft observed was 3.3 instead of 21.5. The correctness of this statement can be checked if 100 or more observations can be taken upon a single particle. The only data available at present is that taken upon different particles. In curves 12 and 13 (Fig. 5) is shown the comparison between the calculated and observed distribution of t and t'. The smooth curve is the theoretical distribution of the times of fall for a single particle having the average size of those recorded in Ehrenhaft's Table V., while the broken curve gives the observed distribution as taken from this same table. As we would expect there is no such agreement as when the observations are all taken upon the same particle, but the theoretical variation of the values of t and t' is amply sufficient to explain all of Ehrenhaft's irregular values of e. It also indicates that the low value of e is probably due to an error in the density, but this can not be shown conclusively until more observations are taken upon a single particle.

To show the relation of Przibram's work to the present theory a

[1] Due to some minor corrections this value does not agree exactly with the value given in the preliminary report.

[2] Phys. Zeit., XI., 1911.

somewhat different treatment may be used because he obtained two[1] values of t and t' for the same particle. A calculation of the times of fall shows that the variation is not as large as that shown in his tables which only means that the particles were of different sizes. But an idea of the differences in two successive times of fall may be obtained by computing the variation for his average-sized particle.

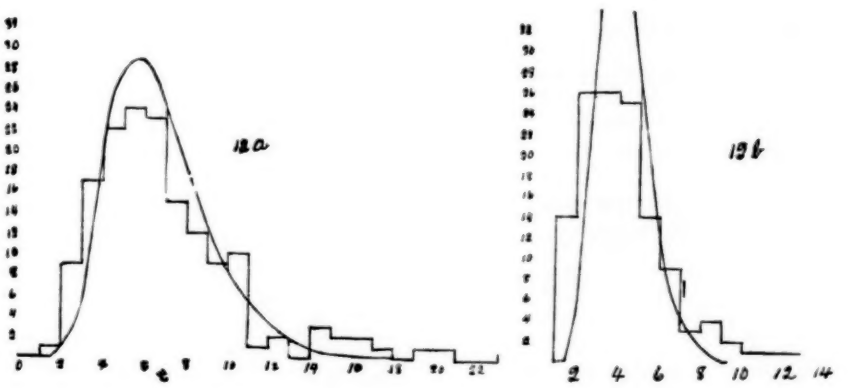

Fig. 5.

For 220 observations taken upon "Phosphornebel" (Table V. of his work) the average time of fall through .0416 cm. is 15.2 seconds. Then

$$V = .00275, \quad a = 44.4 \times 10^6 \text{ cm.}, \quad k = .85, \quad h = 78 \times 10^4,$$

which gives for the probability that a time of fall will be between t_1 and t_2 the equation

$$P = 1.374 \int_{t_1}^{t_2} \frac{t_0 t^{-\frac{3}{2}} + t^{-\frac{1}{2}}}{2} \cdot e^{-\frac{78}{t}(4.15 - 27h)^2} dt.$$

The following values of P were calculated by this formula:

TABLE XI.

t_1	t_2	P
12	13	0.024
13	14	0.13
14	15	0.31
15	16	0.32
16	17	0.17
17	18	0.04
18	19	0.004

[1] Recently both Ehrenhaft and Przibram have taken several observations on a single particle but the number is still too small to make it possible to apply stat stical formulæ.

The probability that any two times occur successively is the product of the probabilities that they will occur separately. For example, the probability that a time between 14 and 15 is followed by a time between 16 and 17 is $.31 \times .17 = .053$. When such a combination occurs the per cent. of difference lies between 14 and 21. Out of 110 double observations 5 or 6 should show a difference of 14 per cent. to 21 per cent. due to the above combinations. Taking all possible combinations the following are obtained:

Between	0	per cent.	and	7	per cent.	about	45	observations.		
"	7	"	"	"	14	"	"	"	37	"
"	14	"	"	"	21	"	"	"	20	"
Above	21	"	"					"	10	"

By calculating the per cent. of difference in two successive times of fall from Przibram's Table V. we have

Between	0	per cent.	and	7	per cent.		55	observations.		
"	7	"	"	"	14	"	"		26	"
"	14	"	"	"	21	"	"		16	"
Above	21	"	"						13	"

The agreement is sufficiently good to show that by the Brownian movement theory we can account for the differences which he obtained. Also these differences are sufficient to show why he obtained an overlapping of the values of $1e$ and $2e$ or $2e$ and $3e$, etc.

Conclusion.

It has been shown that:

1. The continual agitation of a small particle suspended in a gas, known as Brownian movements is entirely explained by the kinetic theory of gases, both qualitatively and quantitatively.

2. The value of Ne obtained from gaseous ionization is the same as that obtained from electrolysis.

3. The irregular values of e apparently resulting from the work of Ehrenhaft and Przibram are entirely explained by the Brownian movement theory.

For this work I am much indebted to Professor R. A. Millikan, who has worked with me while all of the above data were taken, and under whose personal direction this research has been done, and also to Professor A. C. Lunn for his aid and helpful criticism on the first part of this work.

Ryerson Physical Laboratory,
April 25, 1911.

THE RADIANT EFFICIENCY OF ARC LAMPS.

By Henry Phelps Gage.

THE object of the present investigation was to determine the radiant efficiency and the mechanical equivalent of the light from the right angle carbon arc and the Bremer flaming arcs.

The symbols used in this paper are:

R = total watts radiated.

L = light energy; watts of radiant energy of wave-lengths visible to the eye.

W = radiant energy of wave-lengths to which water is transparent.

The ratios here determined are called:

L/R = radiant efficiency.

W/R = "water-bath" efficiency.

Discussion of the Limits of Visibility.

When determining radiant efficiency by an integration method such as that of Langley[1] or of Ångström,[2] certain arbitrary limits are chosen to divide the visible from the invisible parts of the spectrum. These methods are based on the following definition of radiant efficiency.

$$\text{Eff.} = \frac{L}{R} = \frac{\int_{\lambda_1}^{\lambda_2} I d\lambda}{\int_0^{\infty} I d\lambda} = \frac{\text{energy visible part of spectrum}}{\text{total energy radiated}},$$

where I is the intensity of the light and λ_2 and λ_1 are the upper and lower limits of visibility respectively. For most light sources the energy in the ultra-violet is so small that the lower limit λ_1 can be taken as zero with no appreciable error, the energy of the infra-red is however so great that a slight change in the position of the limit in the red causes a great change in the value of L.

Langley,[3] the first to use the integration method, chose the limit .70μ.

Later workers moved the limit of integration far beyond this point to the A line, .76μ.

[1] Science, June 1, 1883.

[2] Phys. Rev., 17, 302, 1903.

[3] Phil. Mag., 30, 260, 1890.

P. G. Nutting[1] criticizes this as being too far from the natural physiological limit, but suggests no other.

While the human eye will respond to radiation of wave-length .76μ and under favorable conditions to even as great wave-lengths as .82μ,[2] this response is very slight. Hence it was thought advisable to choose a new limit which, while arbitrary, would correspond reasonably well with the physiological limit of the human eye.

The principle adopted was that the limit should be so chosen that all light beyond the limiting wave-length should be so small as to be negligible in comparison with the total light.

König and Brodhun[3] have shown that if a white surface is illuminated by two patches of light side by side whose intensities differ by 1.6 per cent. the difference can only just be detected. Therefore in choosing the limit it would appear that the rejected light may be as great but should not be greater than 1.6 per cent. of the total.

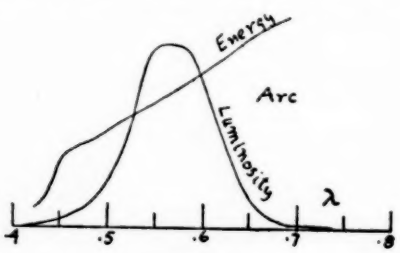

Fig. 1.
Luminosity curve from Abney and Festing.

In the spectrum of the positive crater of the carbon arc, for example, there is almost no visible light beyond .70μ, but in this region the energy is very intense. The result is that changing the limit from .70μ to .76μ increases the energy enormously while hardly changing the visual effect at all; conversely, moving the limit from .76μ to .68μ results in a decrease in energy out of all proportion to the decrease in light.

The choice of a new limit was made by integrating luminosity curves. The total area of such a curve was taken as the total luminosity and the area beyond different wave-lengths was measured with a planimeter. The ratio of the small area beyond the given wave-length to the total area would be the amount of light lost if all radiation of greater wave-length were removed. Such measurements were made on a luminosity curve of Abney and Festing[4] (Fig. 1), on the red sensation curve of König[5] and on some curves of my own. The results expressed in curve form (Fig. 2) indicate the percentage of the total light lost if the red end of the spectrum were removed to the given wave-length.

[1] Electrical World, Vol. 51, p. 1371.

[2] The strong infra-red line of the sodium arc, see Becquerel, Comptes Rendus, Vol. 97, p. 73.

[3] Sitzungsberichte der Königlichen Baierische Academie der Wissenschaft, Berlin, pp. 917–931, 1888, II. Also table in Bulletin of the Bureau of Standards, Vol. 5, p. 286.

[4] Phil. Trans., 177, 423, 1886.

[5] Zeit. Psy. Phys. des Sinnesorgane, 4, 312, 1893. Also Gesammelte Abhandlung, p 286.

From these data and from the general appearance of the spectrum it was decided to use as the limit in the red .68μ. The curves show that with this limit the light removed is less than 1.6 per cent. of the total.

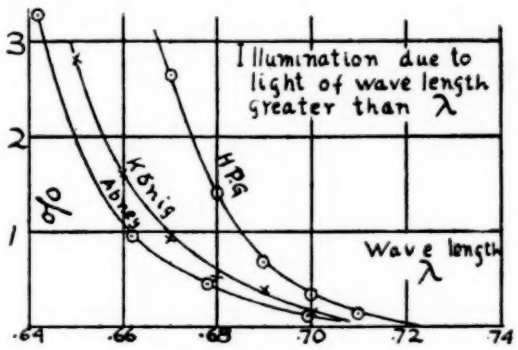

Fig. 2.

The limit is easily located in the arc spectrum of a mixture of lithium and potassium, being nearly half way between the lithium line .671μ and the potassium doublet .691μ. Also the absorption spectrum of neodymium shows a dark line at .68μ.

The limit in the violet could be determined in the same way but is of no great importance, as the energy of the ultra-violet part of the spectrum with most sources is so small that it can safely be neglected. In the study of the arc however it seemed advisable to arrange the apparatus to remove all radiation less than .4μ, thus allowing the cyanogen band of the carbon arc at .42μ to pass but excluding that at .388μ. Between these two bands there is practically no light.

Apparatus.

In the work to be described a modification of the method of Ångström was used. The apparatus was similar to his, the main difference being

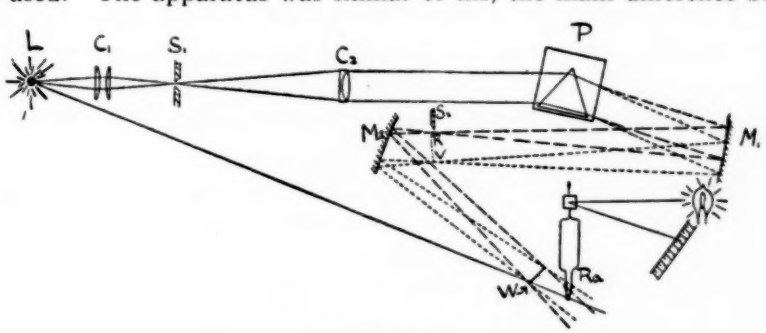

Fig. 3.
Arrangement of apparatus to measure L'/R.

that Ångström used two separate sources of light, one being dispersed into a spectrum, the energy of the other being measured direct; while in the present apparatus both the direct and the modified light come from the same source.

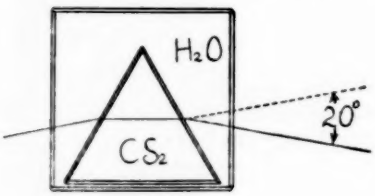

Fig. 4.
Compound prism.

Energy from the source L (Fig. 3) can reach the thermo-junction of the radiomicrometer Ra by either of two paths, (a) direct, no absorption except by air, (b) through the prism train P.

Light from the source is focused by the condenser C_1 on the adjustable slit S_1, is rendered parallel by the lens C_2, dispersed by the prism P and focused as a spectrum at R–V by the mirror M_1. The screen S_2 is placed in the red end of the spectrum so that it cuts off all of the infra-red to .68μ. The mirror M_2 reassembles the spectrum to a patch of white light at the radiomicrometer.

The intensity of the patch of direct light is fixed by the brightness and distance of the source L, but that of the other patch W can be varied by widening or narrowing the slit S_1 until it is of the same brightness as the direct light.

The prism consists in a 60° hollow prism of carbon bisulfide immersed in a square glass cell filled with distilled water. It gives a good dispersion with a deviation of but 20° from a straight line (Fig. 4).

The lenses are of glass.

The mirrors are plano-concave lenses, silvered on the concave side. The focal length of M_1 is 50 cm. and of M_2 is 25 cm.

THE RADIOMICROMETER (Fig. 5).

The suspension of the radiomicrometer was of no. 36 copper wire free from iron, to the bottom of which was soldered a small thermo-junction of bismuth and antimony. To the top of the loop was fastened a piece of silvered cover glass and the whole was suspended by a quartz fiber.

The radiomicrometer was provided with two windows. The one which faced the light had no glass in it in order not to absorb any energy, the one which faced the other way was so placed that the light source could be seen through the instrument. This window was covered with a plane glass.

The junction (Fig. 6) was made by cementing a rod of bismuth and one of antimony to a piece of mica with sealing wax and making connection between them at one end with fusible metal. The free ends were soldered

to the copper loop with fusible metal and the junction dipped into dead black japalac. To get the small rods or wires of bismuth and antimony the metal was melted in a glass tube and the tube drawn down to capillary size. When cold this left the bore of the tube filled with a fine rod of the brittle metal. The ends of the metal were tinned with ordinary solder and then with Woods' fusible metal. It was then an easy matter to solder these rods which were left within the glass together and to the tinned ends of the copper loop.

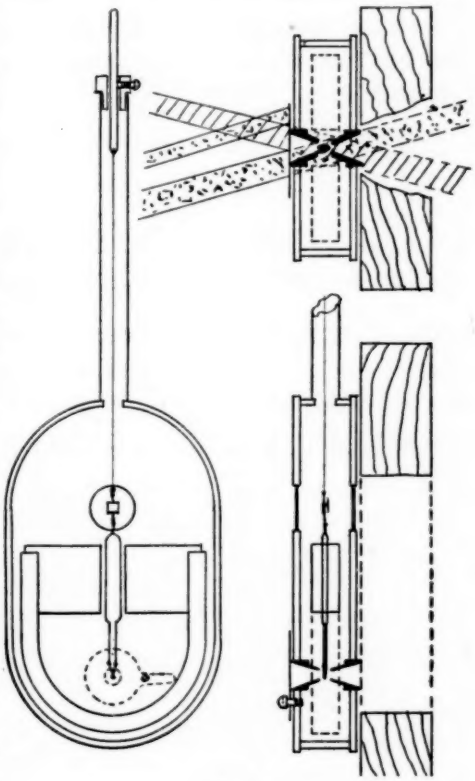

Fig. 5.
The radiomicrometer.

CALIBRATION.

The radiomicrometer used in this work did not need to be very sensitive as the energy to be measured was comparatively large. The ballistic method was used: the farthest point reached on the first swing being recorded in all cases.

To determine whether there was selective absorption by the black japalac surface of the junction, the ratio of W/R was determined for the positive crater of the carbon arc using a Sullivan galvanometer and a lecture room thermopile whose surfaces were covered with different substances: (1) camphor soot, (2) black japalac, (3) dull yellow shellac. The value of W/R came out nearly the same in all cases showing the proportion of energy absorbed to be nearly the same in the visible as in the invisible parts of the spectrum.

Fig. 6.
Radiomicrometer junction.

The scale of the radiomicrometer was calibrated by an acetylene flame moved to different distances. This showed that the "kick" and the steady deflection were proportional to the incident energy. Merritt has shown that the ballis-

tic throw is proportional to the steady deflection both by experiment[1] and by theory.[2]

The radiomicrometer was also calibrated roughly in absolute units by a Hefner lamp and by a Nernst glower. The radiation of the Hefner lamp was taken from Ångström[3] as 11.3 watts.

Example:

Distance Hefner.	Kick.	Kick $\times d^2$.	For 1 Watt: Kick $\times d^2$.
35 cm.	7.42	9,100	808
50	3.75	9,400	832
			820

This value was checked by a Nernst lamp.

Input filament. 100 volts, 1.07 amps. = 107 watts; Radiation, mean spherical, 107 watts; Equatorial, 136 watts $\left(\frac{4}{\pi}\text{ times mean sph.}\right)$; Distance 100 cm.; Kick 12.5; $\frac{\text{kick} \times d^2}{136} = 920$. This is in general argeement with that obtained with the Hefner but is slightly greater as might be expected owing to the reflection from the heater just back of the glower.

In a similar way the more sensitive suspension no. 2 was found to have a constant of 3,540.

SOURCES.

The Right Angle Carbon Arc.—A simple hand feed arc lamp was used, either carbon of which could be moved separately. The carbons were held in the position shown in Fig. 7. The current was kept constant by feeding the carbons forward whenever the current showed signs of dropping. Soft-cored "Columbia Projector" carbons were used.

Fig. 7.
Right angle arc.

Tests were made using alternating and direct current. With the latter both the positive and negative craters were tried.

In some cases the lower carbon was shaded from the radiomicrometer so only the upper carbon could be seen. This was especially necessary when making measurements on the negative crater. The energy from the cyanogen arc between the electrodes was measured by shading both carbon tips. Both the light and energy from the arc is negligible in comparison with that from the hot tips.

With alternating current an inductor (choke coil) was used instead of a resistor because it furnished a much steadier current.

[1] American Journal of Science, 37, 167, 1889.
[2] American Journal of Science, 41, 422, 1891.
[3] *L. c.*

The Bremer Flaming Arcs.—A lamp was kindly furnished by the late C. J. Toerring. It was made for alternating current and burns 8-mm carbons. An economizer and set of blow magnets caused the arc to take the position shown in Fig. 8. The electrodes used were 8-mm. "Excello" carbons known as "yellow" and "brilliant white."

Fig. 8.
Flame arc.

METHOD.

Photometric Match.—The apparatus was so arranged that light from the source could strike the radiomicrometer after having traversed either of two paths, *i. e.*, either straight or through the prism train.

In front of the suspension was an aluminum shutter covered with a piece of white paper. By using screens with suitable holes the direct light was made to fall at the sides of the reassembled light (Fig. 9). The brightness of the reassembled light could be varied by opening or closing the slit S_1 until it was photometrically equal to the direct light.

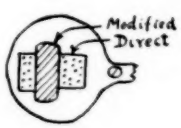

Fig. 9.
White shutter used as photometer.

In making a photometric match the screen was viewed either through a red or a green glass. This was necessary on account of the great brightness of the patches and on account of the slight yellowish color of the mirrors which rendered a photometric match difficult. The energy of the spectrum being greater in the red than in the blue, the match was made through a red glass rather than through a blue glass.

This method gives visual equality at the shutter. The thermo-junction, however, is some distance behind the shutter necessitating a correction.

Call the light falling on the shutter L and R, that striking the thermo-junction L' and R'. The radiomicrometer will then give the ratio of L'/R', not L/R.

$R/R' = D'^2/D^2$, where D is the distance from the source to the shutter and D' that to the junction.

The value of L/L' is obtained by this reasoning:

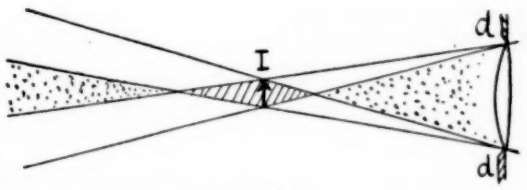

Fig. 10.
Image formation of an extended source.

Suppose I (Fig. 10) to be the image of an extended source of light of uniform brightness with sharply defined edges and d to be a diaphragm. If the radiomicrometer be placed at I or in

tic throw is proportional to the steady deflection both by experiment[1] and by theory.[2]

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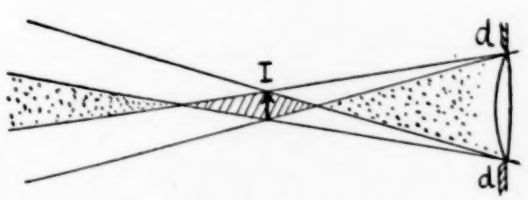

Fig. 10.
Image formation of an extended source.

Suppose I (Fig. 10) to be the image of an extended source of light of uniform brightness with sharply defined edges and d to be a diaphragm. If the radiomicrometer be placed at I or in

the shaded area in the neighborhood of I it will receive light from the entire area of the diaphragm. An eye placed at this point will see the entire opening of the diaphragm lighted with the intrinsic brilliancy of the image I of the source. In this case as far as illumination is concerned the behavior is just the same as though there were an extended source of light at the diaphragm with the intrinsic brilliancy of I. Within the shaded area the energy will follow the inverse square law the distance being measured from the *diaphragm*. Outside the shaded area but within the dotted area the energy will follow the inverse square law but the distance must be measured from the *image* I, for now the radiomicrometer will receive light which has either passed through all parts of I or which would pass through all parts of I just as it would if I were the original source.

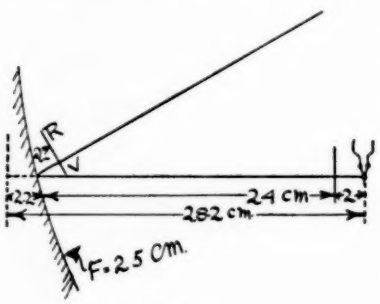

Fig. 11.

Position of diaphragm (R–V) for correcting L'/R.

In the case of the experiment the radiomicrometer was placed in the shaded area (light struck it from all parts of the diaphragm) and the position of the diaphragm was at the focus of the spectrum where the cut off screen was located. The *apparent* distance of the diaphragm was used.

Apparent distance of diaphragm (R–V, Fig. 11) to mirror ..... 2.2 cm.

$$\frac{1}{2} - \frac{1}{25} = \frac{1}{2.2}$$

Apparent distance of diaphragm to screen ..... 26.2 cm.
Apparent distance of diaphragm to junction ..... 28.2 cm.

$$\text{Ratio } \frac{L}{L'} = \frac{d'^2}{d^2} = \frac{28.2^2}{26.2^2} = 1.16$$

Distance of source to screen ..... 107 cm.
Distance of source to junction ..... 109 cm.

$$\frac{R}{R'} = \frac{D'^2}{D^2} = \frac{109^2}{107^2} = 1.03,$$

$$\frac{L}{R} = \frac{1.16}{1.03} \times \frac{L'}{R'} = 1.12 \times \frac{L'}{R'}.$$

In view of the great amount of work previously done by the method of the water cell it seemed desirable to examine the "water-bath" efficiency of the sources as well as the true radiant efficiency. Moreover,

the latter is often difficult to measure directly as L is so small compared to R that it cannot be measured accurately. In this case the ratio of L/W was found as an intermediate value and multiplied by W/R to get the value L/R. L/W was determined in exactly the same way as L/R except that an 8-cm. water-bath was put in the path of the direct ray.

The "water-bath" efficiency is the ratio of the energy to which water is transparent to the total amount of energy radiated. The observed value W'/R is subject to two corrections.

1. The non-selective absorption and reflection of the water-bath. Photometric tests show this to be about 10 per cent. of the incident light.

2. The water-bath makes objects seen through it appear nearer by a distance of one fourth its thickness, 2 cm.

In cases where L/R is determined both directly and indirectly the two results may not quite agree. When this occurs the values are adjusted to divide up the error between them.

The Location of the Cut-off Screen.—There are two methods of locating the cut-off screen:

By looking through the window behind the radiomicrometer the spectrum R–V can be seen. When using a source with a discontinuous spectrum such as the yellow flame arc the screen can be placed in the spectrum till its edge lies just beyond the last visible band, thus allowing all visible but none of the invisible radiation to pass. The spectrum of a white source can be made to appear as if it were discontinuous by placing a solution of a didymium salt before the slit S_1. A solution of crude "cereum oxide" containing about 20 per cent. didymium oxide was dissolved in hydrochloric acid and showed the following rather sharp absorption bands:

.680μ, .622μ, .578μ, .532μ, .520μ, .482μ, .476μ, .444μ, .427μ and transmission bands at .837μ and .770μ.

A spectroscope may be set up to examine the light passing through the radiomicrometer window. With a continuous spectrum the position of the cut-off screen can be followed with the spectroscope, and it can thus be moved to the correct position.

With point sources such as the carbon arc the cut off was very sharp, with discontinuous spectra like that of the yellow flame arc there is a wide dark space between the visible red and the infra-red, but with white extended sources such as the white flame arc the cut off is not sharp but may extend from .66μ to .7μ. This is because of the great slit width necessary.

Readings.—The radiomicrometer was used in connection with a lamp and scale. The scale was first set so its zero coincided with the image

of the lamp filament, then by removing a screen the radiomicrometer junction was exposed to the radiation which it was desired to measure. The radiation was allowed to fall upon the junction until the instrument had reached the farthest point on the first swing, which was recorded. The screen was replaced at leisure. This is a much quicker procedure than to wait until the instrument has settled down to the final steady deflection.

The radiomicrometer was exposed alternately to the direct and to the modified radiation from the source. After ten readings of each had been made the photometric balance was readjusted and another set was made. In this way the effect of any drift in the radiant energy of the light from the source could be eliminated.

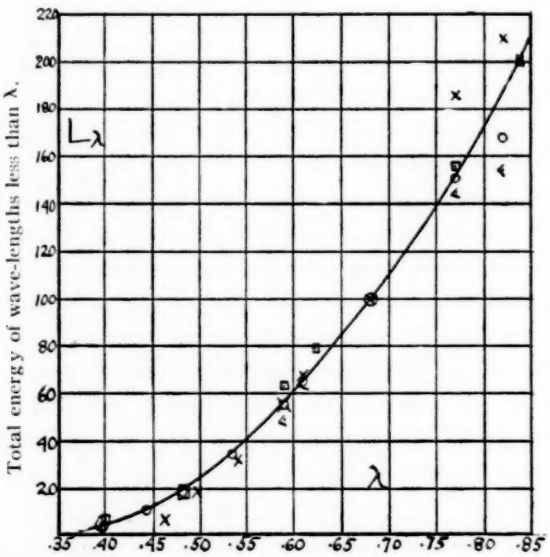

Fig. 12.

Besides the measurements of efficiency, determinations were made of the distribution of energy in the different parts of the visible spectra of the yellow flame arc, and the positive crater of the carbon arc. In both cases the determinations were made as for the measurement of L except that instead of comparing L with R, L was measured with different positions of the cut off screen. The results for the distribution of energy in the different bands of yellow flame arc are included in Table X. The distribution is such that three fourths of the visible energy is due to the red band and one fifth is due to the green band. The results with the positive crater are shown in Fig. 12, which is a curve between the limiting

wave-length and the total energy made up of waves whose lengths are less than the limiting value.

The Mechanical Equivalent of Light.—To determine the mechanical equivalent of light it is only necessary to know the candle power of the source and the watts energy delivered within the limits of the visible spectrum. The data obtained include these values. The mechanical equivalent of light and its reciprocal, the light equivalent of radiation, will be found in Table XIII. These values for the light equivalent of radiation (21 to 39 candles per watt) are so much larger than those found by some of the previous workers that an experiment was made to determine directly what the value should be. As has been mentioned elsewhere Ångström's results recalculated on a basis of .68μ for the limit of visibility gave an efficiency of 21.3 candle power per watt for the Hefner lamp.

Charles V. Drysdale[1] examined the mechanical equivalent of white light from the arc lamp, from the Nernst filament, and also of yellow-green light. His values are 12.4, 8.4, and 16.7 candle power per watt.

P. G. Nutting[2] obtained a value of 13 candles per watt for yellow-green light but did not describe his method.

For the direct determination of the mechanical equivalent of light the assumption was made that an 8-cm. water-bath filled with a copper sulphate solution would transmit only visible light. The apparent candle power of the Nernst filament when viewed through this copper sulphate bath was determined, also the energy transmitted.

Apparent candle power through 8 cm. copper sulphate bath.....26.4 C.P.
Nernst filament 22.5 cm. from radio-micrometer, shining through bath. (Acts as if 20.5 cm. from instrument.)
Deflection.....1.3 cm.
Energy .....665 watts,
giving a value of .0252 watt per candle or 39.5 candles per watt. The color of the transmitted light is bluish green.

[1] Proc. Roy. Soc., 80a, p. 19, 1907.
[2] Electrical World, 51, 1371, 1908.

VALUES OBTAINED WITH THE RIGHT ANGLE ARC.

The Positive Crater.

TABLE I.

Values by the prism train apparatus. Current 10 amperes.

	W' Direct through Water-bath.	L' Through Prism.	L'/W' Per Cent.	L/W Per Cent.	Correction.
1	34.25	12.86	37.5	41.8	×1.105 to
2	37.41	13.90	37.1	41.5	×1.12
3	39.42	11.21	28.5	31.9	
4	34.27	12.45	36.3	40.7	
5	41.82	14.06	33.6	37.7	
6	44.48	17.36	39.1	43.8	
7	41.14	16.90	41.1	46.0	
8	37.54	14.32	38.2	42.2	
9	35.82	13.79	38.4	42.5	
10	35.84	13.41	37.4	41.3	
11	42.97	17.55	40.9	45.5	
12	36.08	17.32	48.0	53.8	
13	34.86	13.30	38.0	42.6	
14	52.90	23.10 (13 amps.)	43.7	48.7	
				42.9	

TABLE II.

Photometric measurements of arc.

Volts.	Amperes.	Watts.	Candle Power.	From Energy Input.	
				Watts per Candle.	Candles per Watt.
55	7.5	410	1,550	.265	3.8
	10	550	2,300	.240	4.2
	15	830	3,850	.215	4.65
	20	1,100	5,600	.195	5.1

TABLE III.

Results with water-bath.

Amperes.	Radiomicrometer Reading.		W'/R Per Cent.	W/R Per Cent.	Correction.
	R	W'			
7.5	12.43	2.11	17.0	18.5	×1.09
10	16.08	3.2	19.9	21.7	
15	21.86	5.26	24.1	26.2	
	27.48	6.79	25.4	27.6	
	22.72	5.70	25.1	27.3	
	24.45	5.94	24.3	26.5	
	24.47	6.09	24.9	27.1	
	24.72	6.02	24.3	26.5	
	21.23	5.36	25.2	27.5	
	23.52			26.96	
20	33.04	8.71	26.3	28.7	

The Negative Crater.

TABLE IV.

L/W' Estimated.	W/R	L/R
40%	8.25%	3.3%

The Right Angle Arc; Alternating Current.

TABLE V.

Results with the prism train apparatus. Current 15 amperes.

W'	L'	L'/W' Per Cent.	L/W' Per Cent.	Correction.
20.78	8.2	39.5	44.2	× 1.12
17.44	6.34	36.3	40.7	
19.98	6.91	34.6	38.8	
18.94	6.78	35.8	40.1	
18.52	6.51	35.1	39.4	
			40.64	

TABLE VI.

Candle power measurements.

Volts.	Amperes.	Watts.	Candle Power.	From Energy Input.	
				W.P.C.	C.P.W.
50	15	750	700	1.07	.94
50	20	1,000	1,200	.83	1.2

TABLE VII.

Results with water-bath.

Amperes.	R	W'	W'/R Per Cent.	W/R Per Cent.	R Watts Radiated.
		Lower carbon shaded.			457
15	9.37	1.53	16.4	17.77	618
20	12.66	2.44	19.25	20.9	
		Lower carbon unshaded.			590
15	12.08	1.74	14.36	15.61	
		Arc between the craters.			6.5 watts
	1.67	.335	20	21	.85 per cent. of crater

TABLE VIII.

The yellow flame arc. Entire arc.

L/*W*	*R*	*W'*	*W*/*R*	Correction.
50.4	46.8	12.51	29.2	× 1.087
54.1	50.86	12.25	26.1	Suspension constant
68.9	52.32	12.98	27.0	3,540 divs. per
60.8	56.35	12.56	24.0	watt at one cm.
55.8	53.62	13.16	26.6	
52.6	52.1	13.59	28.4	
64.5				
55.3				
55.7				
52.9				
57.1	52.0		26.9	R=430 watts

From Energy Input.

Amperes	13.5	Watts per candle	.23
Volts	44.5	Candles per watt	4.3
Watts	600		
Candle power	2,580		

TABLE IX.

The yellow flame arc. Arc stream.

L/*W* Per Cent.	*W*/*R* Per Cent.	*L*/*R* Per Cent.	*L*/*R* Calculated.
78.5	48.5	35.8	
		39.8	
76.0	47.0	32.5	
		47.5	
73.5	49.7	45.9	
		45.6	
72.1	49.3	49.1	
		35.4	
78.8	50.5		
81.0			
Found 76.8	49.0	41.45	37.60
Adjusted values 79	49.5	39	

TABLE X.

Distribution of energy in the different bright bands of the spectrum of the arc stream.

100 *per cent. is the energy of the visible part of the spectrum.*

Energy which gets through water-bath	126 per cent.
Luminous energy; red + blue + green	100
Green + blue	25.5
Blue	5.0
Green	20.5
Red	74.5
Infra-red (which gets through water-bath)	26
Red + infra-red	100.5

TABLE XI.

The white flame arc. Entire arc.

L/W Per Cent.	R	W'	W'/R Per Cent.	W/R Per Cent.	Correction.
44.4	56.93	16.28	28.6	31.1	×1.087
45.7	59.45	17.41	29.4	32.0	
45.3	57.35	16.42	28.7	31.2	
47.3	56.72	16.94	29.9	32.5	
46.0	57.76	17.14	29.7	32.3	
45.58	57.64	=476 watts		31.82	

		From Energy Input.	
Amperes	13.5	Watts per candle	.44
Volts	47	Candles per watt	2.27
Watts	635		
Candle power	1,440		

TABLE XII.

The white flame arc. Arc stream only.

L/W Per Cent.	W/R Per Cent.	L/R Per Cent.	L/R Calculated. Per Cent.
54.3	50.5	27.85	27.4
Adjusted values 54.5	50.5	27.5	

Probable Accuracy of Results.—No very exact results with arc lamps are possible on account of the wide fluctuations continually occurring in their behavior, hence it is necessary to be content with a rather rough approximation.

With the apparatus used in the present investigation there are apparently no inherent instrumental errors of greater magnitude than the settings for photometric equality.

ÅNGSTRÖM'S RESULTS.

In his paper on "Energy in the Visible Spectrum of the Hefner Standard,"[1] Ångström determined the following:

The distribution of energy in the infra-red.

The percentage of the total energy of wave-length less than .76μ; L_{76}/R.

The value of L_λ for various wave-lengths. (The energy of the light of all wave-lengths less than λ.)

From this, the distribution of energy in the visible part of the spectrum.

These last two were expressed in the form of curves.

[1] PHYS. REV., 17, 302, 1903, Nova Acta, Royal Society of Science, Upsala, 3d series, Vol. XX.

TABLE XIII.

Summary of results.

Source.	Amps.	C.P.	L/W Per Cent.	W/R Per Cent.	L/R Per Cent.	Watts.		As Radiated.		At 100% Eff.	
						R	L	W.P.C.	C.P.W.	W.P.C.	C.P.W.
Carbon arc	7.5	1550		18.5	7.9	607	48	.39	2.6	.031	32
	10	2300	42.9	21.7	9.3	785	73	.34	3.0	.032	31
+ Crater....	15	3850		27.0	11.6	1148	133	.30	3.4	.035	29
	20	5600		28.7	12.3	1614	199	.29	3.5	.036	28
											30
−Crater		(est.)	40	8.25	3.3						
A. C.											
Shaded....	15	700	40.7	17.8	7.2	457	33	.65	1.5	.047	21
	20	1200		20.9	8.5	618	53	.51	2.0	.044	23
Entire	15	700		15.6	6.3	590	37	.84	1.2	.053	19
											21
Arc stream..				21		6.5					
Flame arcs											
Entire arc											
Yellow	13.5	2580	57.1	26.9	15.4	430	66	.17	6.0	.026	39
White.....	13.5	1440	45.7	31.8	14.6	476	69	.33	3.0	.048	21
Arc stream											
Yellow....	13.5		79	49.5	39						
White.....	13.5		54.5	50.5	27.5						
Nernst through copper sulphate		26.4			100		.665			.025	39.5
Hefner (Ångström)		.9			.363	11.3	.032	12.3	.08	.047	21.3

The value of L_{76}/R for the Hefner is .96 per cent.

By reference to the curve the value of L_{68}/L_{76} is .389, giving L_{68}/R = .373 per cent.

The total radiation at the distance of one meter is 214×10^{-7} calories per square centimeter per second.

Assuming uniform spherical distribution this gives a value of 11.28 watts as the total radiation.

The value L_{76}/R = .96 per cent. gives for the mechanical equivalent of light .1085 watt per Hefner, .1205 watt per candle[1] or 8.3 candles per watt.

The value of L_{68}/R = .373 per cent. gives .0422 watt per Hefner, .0469 watt per candle or 21.3 candles per watt.

Although the removal of the light between .76μ and .68μ has a large effect on the energy radiated it has but a slight effect upon the illumination given by the lamp.

[1]Hefner = .9 candle power.

The author wishes to express his appreciation of the facilities offered by the department of physics and his gratitude for the help and encouragement given by his fellow students and by the staff.

Summary.

The *A* line .76μ is not a suitable point to take for the limit of the visible spectrum.

Examination of luminosity curves shows that it would be preferable to assume this limit to be at .68μ.

If all radiation of greater wave-length than .68μ be removed the resulting decrease in light can be neglected.

The measurement of radiant energy was made with a radiomicrometer. The kick or ballistic method was used. The kick is proportional to the final deflection and to the energy.

The calibration of the radiomicrometer in absolute units using the Nernst filament and the Hefner lamp showed a general agreement between the energy of the Nernst filament as calculated from the energy input and as derived from Ångström's value of the radiation from the Hefner lamp.

A modification of the method of Ångström was used to determine the radiant efficiency of the right angle carbon arc, the yellow flame arc, and the white flame arc.

The greatest efficiency was found in the arc stream between yellow flame carbons, the carbon tips being shaded. With this arc the light energy constitutes 39 per cent. of the energy radiated.

The highest efficiency from black body radiation is from the positive crater of the carbon arc. An efficiency of from 8 to 12 per cent. may be expected from this source.

Calculations of the mechanical equivalent of light from these data show that one watt can produce as high as 30 candle power of white light and 39 candle power of orange light (yellow flame arc). This is much higher than has been previously supposed except from the data of Ångström which give 21.3 candle power per watt when recalculated for the limit .68μ.

Cornell University,
Ithaca, N. Y.,
June, 1911.

THE TRANSMISSION OF SOUND THROUGH POROUS AND NON-POROUS MATERIALS.

BY C. S. McGINNIS AND M. R. HARKINS.

THE object of this investigation was to study more extensively the nature of sound transmission through porous and non-porous materials and to quantitatively determine the transmitted intensity. Up to the present time little attention has been given to the experimental phase of the subject. It was determined in 1901 by Tufts[1] that "The resistance offered by granular materials to the to-and-fro motion of the air particles in a sound wave is proportional to the thickness of the material, other things being equal." Also "Observations were made upon the transmission of sound and of direct currents of air through porous materials of a woven texture. The results showed that the resistance which such materials offered to the transmission of sound and direct currents of air was directly proportional to the thickness or number of layers of the material used, as was the case with granular materials."

Weisbach[2] working along similar lines arrived at the following conclusion: The acoustic transmission and reflection of thin sheets are not easily measured because the vibrations of the sheet as a whole often complicate and obscure the sound otherwise transmitted. If one eliminates these swings, as far as possible, then one arrives at a result which agrees with theory, namely, that the transmission and reflection for given wave-lengths depend only on the mass per unit area of the sheet.

APPARATUS.

The source of sound was an open organ pipe, pitch 768 complete vibrations, with pressure supplied by a motor-driven centrifugal blower and controlled by a pressure regulator. In the path of the stationary sound waves was placed a telephone receiver P, which was connected through a capacity C, to the primary of a transformer T.

The secondary of the transformer was connected in series with a resistance R, a Siemens and Halske direct current, high sensibility gal-

[1] Transmission of Sound through Porous Materials, Am. J. of Sc. (4), 11, 1901, p. 357.

[2] Versuche über Schalldurchlässigkeit, Schallreflexion, und Schallabsorption, Ann. d. Phys., 14, p. 763, 1910.

vanometer G, and a crystal rectifier M. This sound detector was devised by G. W. Pierce.[1]

Preliminary experiments showed conclusively that a telephone transmitter with battery, although extremely sensitive, could not be relied upon for quantitative results. The telephone receiver, more constant in its action although less sensitive, was therefore employed. A number of receivers were tried before one of sufficient sensitiveness was found. The one finally employed was of the Stromberg Carlson type which was so constructed as to respond best to variation in pressure, that is, at the node of the stationary wave. In order that the sheets of material could be conveniently exposed before the mouth of the receiver and that the incident sound could have no other access to the diaphragm than through the material, the receiver was encased in a thick lead tube closed at one end.

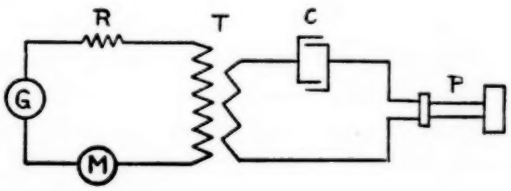

Fig. 1.
Receiving circuit.

A one to twenty step-up transformer gave best satisfaction for the particular constants in the circuit. Its primary resistance was 5.7 ohms and secondary resistance 850 ohms. In order to determine the best magnitude of capacity, a resonance curve was taken. This curve showed that 0.2 micro-farad gave the highest deflection for the particular pitch used.

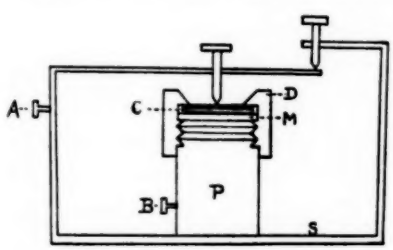

Fig. 2.
Mounting for crystal.

The crystal rectifier mounting, with terminals AB is shown in Fig. 2. A threaded, cylindrical, brass pillar P supports a sheet of mica M, which in turn supports the crystal C. The screw cap D holds the crystal in position. A hard-rubber base S supports the brass pillar and also the two metal posts which carry the regulating screws. A mutual adjustment of these screws produces any desired pressure on the crystal. Crystals of molybdenite proved to give sufficient rectification and were used throughout the research, but satisfactory ones were obtained only after many trials. Even for one particular pressure the percentage

[1] A Simple Method of Measuring the Intensity of Sound, Proc. Am. Acad., XLIII., No. 13, 1907.

rectification did not remain constant for any great length of time, so that it became necessary after each reading to check the original reading by an additional observation. Oftentimes a tedious manipulation of the pressure was necessary to maintain a proper deflection.

CALIBRATION.

The calibration consisted in finding the relation between the intensity of the incident sound and the deflection of the galvanometer. The intensity of the sound source was kept constant by regulating the air pressure which was indicated by a water manometer. The intensity of the sound incident on the diaphragm of the receiver was varied by the use of lead plates containing circular apertures of different diameters. The galvanometer showed no deflection when a lead plate was clamped over the end of the lead casing containing the receiver. The clamping was done as follows: A flat brass ring was permanently fixed to the end of the lead casing. A similar brass ring was screwed to the first one and between them the lead plates were held in position. The circular apertures of the lead plates were small compared to the size of the diaphragm so that allthe energy passing through the openings was incident near the center of the diaphragm. Hence the intensity of the incident sound was directly proportional to the area of the aperture. A reversion to the 3/8-inch aperture after each observation checked the constancy of the crystal. Fig. 3 shows that the deflection of the galvanometer is directly proportional to the area of the aperture and hence to the intensity of the incident sound. For apertures as large or larger than the diaphragm opening the law no longer holds.

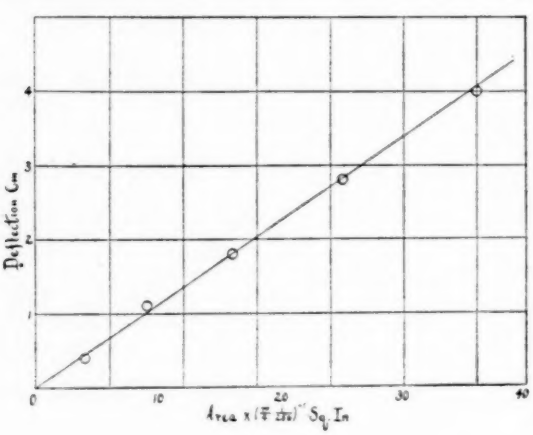

Fig. 3.

Observations and experimental details.

Preliminary experiments showed conclusively that the method of clamping the materials investigated influenced to a high degree the percentage of sound transmitted. A more thorough study of the matter showed that different methods of clamping produced different degrees

of lateral vibrations. Thus a special method of clamping was devised which practically eliminated the lateral vibrations. Until this was done it was impossible to procure results which were independent of the clamping pressure and the tension in the specimen. Fig. 4 shows the clamp employed.

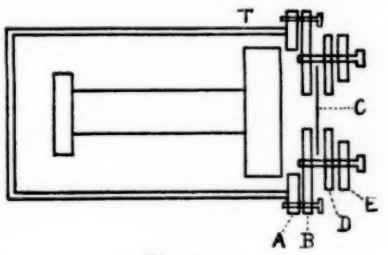

Fig. 4.
Device for damping lateral vibrations.

A is a flat brass ring 0.2 cm. thick and 6 cm. internal diameter which is fastened permanently to the end of the lead tube *T*. *B* is a brass plate 0.15 cm. thick with aperture ½ inch in diameter. *C* is the specimen and *D* is a lead sheet 0.05 cm. thick with ½-inch aperture. *E* is a brass ring 0.35 cm. thick with 1-inch aperture.

Since the galvanometer registered a maximum deflection when the receiver was placed in a node of the stationary wave, that position was employed in all observations. The following substances were investigated, namely, blotting paper, wrapping paper, roofing paper, oil cloth, tin-foil, asbestos, curtain material, lawn, longcloth, percale, cretonne, curtain scrim, linen, calico, felt, velvet, copper wire gauze, mica and aluminum.

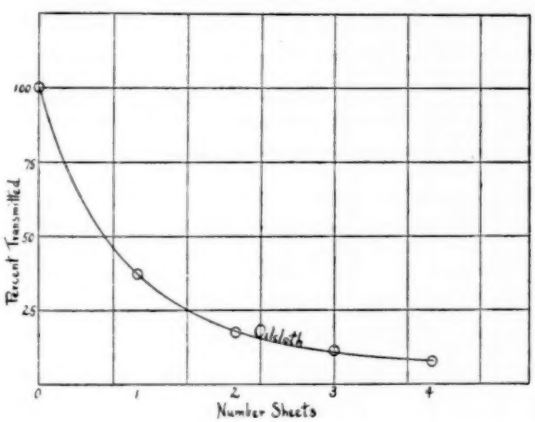

Fig. 5.

In order to explain definitely how the lateral vibrations of the material affected the observations we will confine our discussion to oil cloth which is non-porous, that is, does not allow air currents to pass through. Fig. 5 shows the relation between the percentage transmitted and number of sheets when the apertures in *D* and *E* of Fig. 4 were large, so that the oli cloth was clamped only at the outer edge.

It is to be noted that the percentage transmitted ranges from 37 per cent. for one sheet to 7.5 per cent. for four sheets. When a lead plate was used in place of oil cloth the galvanometer deflection was zero, showing that there were no leaks. Fig. 5 is in very close agreement with results obtained by Weisbach for oil cloth of a similar mass per

unit area, namely, 0.034 gram per sq. cm. When the oil cloth was clamped exactly as shown in Fig. 4 and when the open deflection was 4 cm. as was the case in Fig. 5, the galvanometer showed no deflection, thus indicating that the transmission as shown in Fig. 5 was due to the

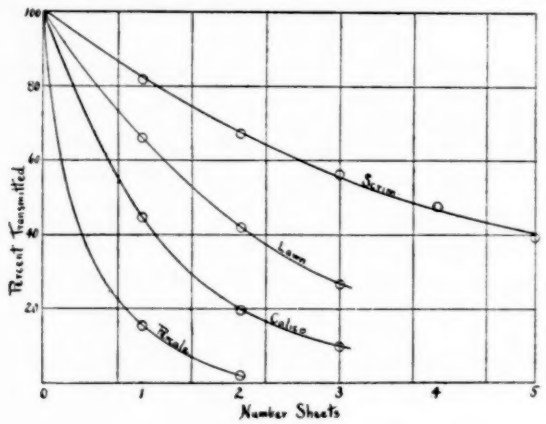

Fig. 6.

oil cloth being set in vibration and acting as an independent vibrating source. This discrepancy is of great significance and will be discussed later. Other non-porous substances or those nearly so, acted in a similar manner. Roofing paper, wrapping paper, asbestos, blotting paper,

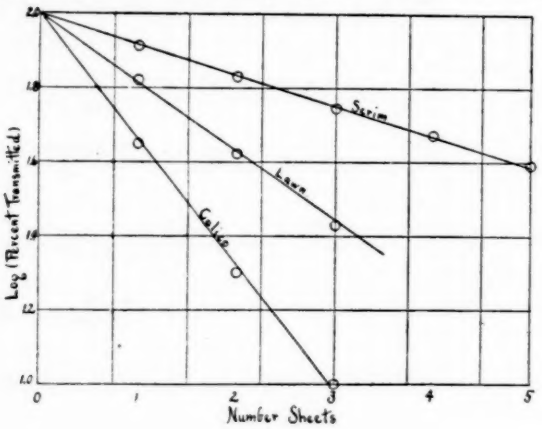

Fig. 7.

curtain material, tin foil, mica and aluminum transmitted either zero or considerably less than one per cent. The more porous substances of woven texture, were used to determine the relation between the intensity transmitted and the number of sheets. Table I. shows the numerical results.

The curves for calico, percale, curtain scrim and lawn, showing the relation between number of sheets and percentage transmitted, are shown in Fig. 6, while the relation between number of sheets and logarithm of percentage transmitted, is shown in Fig. 7.

TABLE I.

Material.	Mass / Area in gms. / cm.²	Per Cent. Transmitted.	Material.	Mass / Area in gms. / cm.²	Per Cent. Transmitted.
Lawn.			*Longcloth.*		
1 sheet	0.00537	65.9	1 sheet	0.00984	27.6
2 sheets		41.8	2 sheets		7.6
3 sheets		26.7	*Cretonne.*		
Calico.			1 sheet	0.0120	27.8
1 sheet	0.00868	44.5	2 sheets		15.5
2 sheets		19.7	3 sheets		11.8
3 sheets		10.0	*Linen.*		
Percale.			1 sheet	0.0129	6.3
1 sheet	0.0121	15.3	*Linene.*		
2 sheets		2.0	1 sheet	0.0167	2.0
Curtain scrim.			*Felt.*		
1 sheet	0.0051	81.6	1 sheet	0.0266	1.6
2 sheets		67.2	*Velvet.*		
3 sheets		56.1	1 sheet	0.0158	1.6
4 sheets		47.5	*Copper wire gauze.*		
5 sheets		39.1	1 sheet	0.102	76.4
			2 sheets		58.6

DISCUSSION OF RESULTS.

It is readily seen from the results that non-porous substances such as oil cloth, paper, tin foil, etc., do not transmit sound when the lateral vibrations are eliminated, at least in so far as our apparatus will detect. This would limit the transmission to a very small fraction of one per cent. Porous substances, on the other hand, do transmit a considerable percentage of incident sound, the percentage depending upon the diameter, length and nature of the channels. Inspection of the materials would lead one to expect a much greater transmission than was found. The general law appears to be

$$I = I_0 e^{-kn}, \tag{1}$$

$$\log \frac{(I)}{(I_0)} = -kn, \tag{2}$$

where I = transmitted intensity,
I_0 = incident intensity,
n = number of sheets,
k = constant.

All substances investigated agreed with this law with the exception of cretonne which proved to be a decided exception. In cretonne the channels are not so definite and clear cut as in the other cases. The exponential form of equation (1) suggests at once that whatever sound is transmitted goes through the pores. This would immediately suggest an investigation of the channel action. Preliminary experiments on a single channel of diameter 3/16 inch, in lead plates, showed that the percentage transmitted, as the length of the channel was changed, agreed with the above law very closely. This matter will be further investigated.

Our results differ widely from those of Weisbach who attempted to apply Rayleigh's[1] formula for the amplitude[2] of the sound reflected from thin plates, namely,

$$-\frac{\frac{\pi\rho_1 l}{\rho\lambda}}{\sqrt{1+\pi^2\left(\frac{\rho_1 l}{\rho\lambda}\right)^2}}, \tag{3}$$

where l = thickness of plate,
ρ = density of first medium,
ρ_1 = density of second medium (plate),
λ = wave-length.

When the first medium is air and the pitch 768 double swings, as used in our experiments, formula (3) may be written

$$I_r = I_0 \frac{\rho_2^2}{.00034 + \rho_2^2}, \tag{4}$$

where I_r = reflected intensity,
I_0 = incident intensity,
ρ_2 = mass per unit area of the plate.

If there is no absorption the transmitted intensity I_t will be $I_0 - I_r$,

$$I_t = \frac{.00034}{.00034 + \rho_2^2}. \tag{5}$$

Weisbach's results did not agree with Rayleigh's theoretical values but could be brought into approximate agreement by shortening the ordinates by a large constant factor. He did not fulfill the conditions imposed by the formula. For a statement of these conditions and a complete interpretation of the formula we are indebted to Baron Rayleigh.

The formula applies to the reflection of plane waves incident normally on a free and thin lamina which lamina is incompressible as compared

[1] Theory of Sound, Vol. II., p. 88.

[2] Note misprint in Rayleigh, Vol. II., p. 88, of intensity for amplitude.

with the first medium and is completely uniform in its mechanical properties. The lamina acts as a body possessing inertia under the pressures of the three waves, incident, reflected and transmitted Experimentally it would be almost impossible to satisfy the requirement of freedom. However a membrane such as oilskin spread over a large enough hoop might possibly satisfy the requirement, *i. e.*, that the motion shall be independent of any tension due to the outside fastening. The vibrations which Rayleigh's formula permits are those controlled by the inertia of the membrane and the elasticity of the air and not those which depend on the elastic constants of the material. Therefore Weisbach should not have applied Rayleigh's formula in any case, since the condition of freedom was not satisfied.

We also wish to emphasize the fact that formula (5) cannot be applied to our results, even to those substances such as tin foil, paper, mica, etc., whose mechanical properties are uniform, since the condition for freedom is not satisfied. In any case it cannot be applied to porous substances. If the lateral vibrations are damped the substances which are uniform in their mechanical properties should act as a fixed wall, namely, reflect all incident sound. This is conclusively shown by our results.

Weisbach's results could not be expected to agree with ours since his membrane was not thoroughly damped while in our case the lateral vibrations were completely eliminated. Our results verify the latter statement. For non-porous substances or those nearly so as paper, oil cloth, curtain material, etc., we found the transmission to be either zero or a small fraction of one per cent., while Weisbach found from 30 to 60 per cent. For porous substances such as linen, calico, lawn, etc., we likewise found a much smaller percentage transmitted.

Summary.

1. The crystal rectifier, with apparatus as described, is reliable when used for the comparison of sound intensities but cannot be used for absolute determinations since the percentage of rectification is liable to change.

2. For non-porous substances or those nearly so, the intensity of sound transmitted is either zero or considerably less than one per cent.

3. For porous substances of woven texture the general law for the transmitted intensity is $I_t = I_0 e^{-kn}$, *i. e.*, each sheet transmits a definite percentage of the sound incident upon it.

4. Most of the sound which is commonly said to be transmitted is due to the lateral vibrations of the material as an independent sound source. The intensity actually transmitted depends upon the size and nature of

the pores, *i. e.*, absorption is the predominating factor. This is in agreement with Tufts' general idea as previously stated, namely, that the transmission of sound depends definitely upon the facility with which the substance transmits currents of air.

In conclusion we wish to thank Professors H. C. Richards and R. H. Hough for their valuable suggestions and coöperation.

Randal Morgan Laboratory of Physics,
University of Pennsylvania,
May 1, 1911.

THE SELECTIVE REFLECTION OF ORTHO-, META- AND PYRO-PHOSPHATES IN THE INFRA-RED SPECTRUM.

By Grace Langford.

IT is well known that the reflecting power of certain non-metallic substances varies widely in different parts of the infra-red spectrum. For example, the reflecting power of quartz[1] is practically zero for radiations of wave-length 7.4μ and rises abruptly to 75 per cent. at 8.45μ. The work of Coblentz[2] and Morse[3] shows that not only may carbonates, nitrates and sulphates be distinguished from each other by their selective reflection alone, but also that of the salts of any one acid, those with the heavier bases may in general be separated from those with the lighter, the valence of the bases being the same in all. There was little evidence on salts having a common acid-forming element to show either the effect of a change in the valence of the base, or the effect of a change in the ratio of the weight of the acid forming element to the weight of oxygen combined with it in the acid radical. The series of substances which seemed best adapted to a study of these effects were not obtainable in a form suitable for examination by the usual methods. This paper describes a method by which one may obtain an indication of the selective reflection characteristic of those salts which cannot be had in large crystals. This method has been applied to the examination of sixteen of the ortho-, meta- and pyro-phosphates, and the results are given in the following pages.

Preparation of Surfaces.

A large number of the phosphates were obtainable only in the form of powder precipitates. A few were in the form of minute crystals and one only, sodium meta-phosphate, in a solid mass. On this last a surface large enough for the purpose was polished by rubbing on a surface of ground plate glass. Since the melting point of most phosphates is very high it was impracticable to melt them into solid cakes. The possibility of obtaining reflecting surfaces by the compression of powders was first suggested by Mr. Eimer, of Eimer and Amend, and the practical details of the following process were devised by Dr. E. F. Nichols and Dr. W. S.

[1] Phys. Rev., 1897.

[2] Investigations of Infra-red Spectrum, Parts III. and IV., 1906; V., 1908.

[3] Astrophysical Journal, 26, p. 225, 1907.

Day. In Fig. 1, B represents a block of hardened and polished steel to which the steel rings, C and C', could be tightly screwed. A is a steel piston, which slips easily in the rings. The ring C contains the powder to be pressed and C' acts merely as a guide for the piston. The steel block was ground with emery and water and polished till the top had a fine mirror surface. The rings having been screwed to the block, the lower one, C, was filled with the powdered salt and the piston inserted on top of the powder. The piston head was then subjected to a pressure of 42,000 to 52,000 pounds per square inch.[1] After releasing the pressure and withdrawing the piston the steel block was carefully separated from the rings, leaving in the lower ring a solid cake of the compressed powder which sometimes had a very brilliant mirror surface copied from the surface of the polished steel block. In some cases a better surface could be formed by forcing the cake out of the ring and carefully polishing it in the ordinary way. The salts used were obtained as free from water as possible. To drive off any moisture which might be held in the precipitates and in the case of Na_3PO_4, to drive off water of crystallization, the substances were heated over a sand-bath. Unless the powder were very fine it was ground in a mortar and after drying was sifted through graded sieves. The finest powder, that passing the 200 per inch mesh, was put in the rings first, that it might form the surface and the coarser parts were used for the main bulk of the cake. When only a small quantity of substance was available it was put in the ring first and the rest of the cake made of a different substance. Only three of the substances used showed any crystalline structure even under the high power microscope. Of these Na_3PO_4 lost its crystalline form with the water of crystallization. The other two, $Zn_3(PO_4)_2$ and KPO_3 remained unchanged when heated.

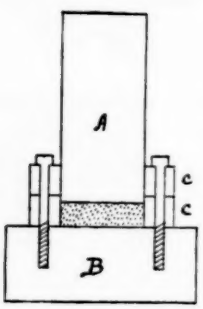

Fig. 1.

The surfaces obtained by pressure against a plane surface in this way were rather convex, probably a result of the bulging of the powder after the pressure was removed. Sometimes the cake cracked, due to the strain. As most of the pressed cakes of the phosphates were not hard enough to be ground plane and polished, an effort was made to reduce the convexity by pressing on a slightly convex steel surface. But as no two surfaces had the same convexity even when the same pressure was used it was impossible to predict just what curvature would result in any

[1] The pressures were obtained at first by the use of the testing machine in the mechanical engineering laboratories through the kindness of Professor Ira H. Woolson and Mr. J. S. Macgregor. Later a hydraulic press was used in the physics laboratory.

given case or to wholly correct it. With these curved surfaces the absolute reflecting power was not obtained. But since other conditions made it impossible and as relative values answer our purpose this lack of planeness was not very important. Also the collecting mirrors used in the examination were large enough to receive the beam even if its divergence were slightly increased by the curvature of the salt's surface. Approximately absolute values might at any time be obtained by determining the values at a few wave-lengths distributed along the spectrum and deducing the whole reflection curve from the relative values at the selected wave-lengths. The cakes of the various substance when pressed differed much in appearance and structure. Aluminum and magnesium phosphates, $AlPO_3$ and $Mg_3(PO_4)_2$, for example, in the form of white powder looked alike. After pressing, the $AlPO_4$ had the appearance of fine white porcelain and was brittle and chipped off in layers like slate, and the surface was very brilliant. But $Mg_3(PO_4)_2$ gave a dull surface and showed no pronounced structure.

General Plan of Apparatus.

The mirror M (Fig. 2) forms an image of the source, N, on the reflecting surface under examination at S. The reflected beam is brought to a focus by the mirror M_2 on the collimator slit C of spectrometer. After passing the slit the beam is rendered parallel by the spectrometer mirror, M_3, and is then resolved by the prism P, and reflected by the plane mirror M_4. The portion of the spectrum falling on the second spectrometer mirror M_5 is brought to a focus on the slit, T, which replaces the usual cross wires of the observing telescope of the spectrometer. The energy passing through the slit falls upon the concave mirror, M_6, and is concentrated on the vane of the radiometer, R.

There are several reasons for forming an image of the source N on the reflecting surface S. In the first place the adjustments are more easily made. Secondly, a smaller surface may be used without loss of energy, and the curvature of the reflecting surface over a small area is likely to be more regularly than over a large one. Moreover, it was possible to choose the best part of the surface, thus avoiding the edges and flaws.

Details of Apparatus.

Source.—A Nernst glower, 110 volts and 0.8 ampere, fed by a 120-volt storage battery served as a source. The glower was protected from air currents by an asbestos shield. An ammeter and variable resistance in circuit made it possible to hold the glower current constant in spite of slow fluctuations in the battery voltage and to detect any sudden

change likely to cause error. After adjustment the current usually remained very constant throughout a series of observations.

Spectrometer.—A Schmidt and Haensch spectrometer with Rubens attachment, belonging to the Rumford Committee of the American Academy of Arts and Sciences was used. In place of the customary simple prism the spectrometer table bore the Wadsworth mirror prism arrangement[1] and the different parts of the spectrum could therefore be caused to fall upon the slit T (Fig. 2) by rotating the prism table, the arms of the spectrometer remaining fixed. The spectrometer mirrors M_3 and M_5 had each a focal length of 35 cm. and an aperture of about 4 cm.

Prism.—The sylvite prism P had faces 3.2 cm. high and 2.5 cm. broad, and a refracting angle of 38° 9′ 51″. Wave-lengths to 20μ may be determined with a sylvite prism of this refracting angle so that the field of observation was extended considerably beyond the limit reached with ordinary 60° rock-salt prism. In order to interpret spectrometer sittings in terms of wave-lengths a curve was drawn with wave-lengths as abscissas and as ordinates, one half the difference between the angles of minimum deviation for the given wave-length and for the sodium line. One half the angle was taken, since with the Wadsworth prism and mirror arrangement the angle of rotation of the prism table is equal to one half the change in the angle of minimum deviation. The values for the angles of minimum deviation for wave-length from .5μ to 20μ at intervals of .5μ were calculated from the Ketteler-Helmholtz dispersion formula using the constants for sylvite determined by Rubens.[2] The adjustment of the spectrometer was repeatedly checked by observing the reading of the spectrometer scale when the B line coincided with the telescope slit. The curve for wave-lengths and spectrometer settings was tested by observing the wave-lengths of maximum reflection for quartz and calcite which agreed within experimental errors with the values found by other observers.

Radiometer.—A Nichols radiometer with a sylvite window was used. The mica vanes measured 5 mm. × .75 mm. and were placed with their outer edges 8 mm. apart. The faces of the vanes were covered with a thin layer of platinum black held on by shellac. The radiometer stood on a shelf supported by a thick inner wall, and under ordinary conditions the vibrations of the building did not affect the readings. Deflections of the radiometer vanes were determined by observing the position of the image of the index lamp, formed on the scale one meter

[1] Phil. Mag., 38, 337, 1894.

[2] Wied. Ann., 60, 418, 1897; 60, 724, 1897.

distant, by a small concave mirror fastened at the lower extremity of the suspended system.

Adjustment of the Surface.—The surface to be examined was clamped behind one of the openings, S_2 (Fig. 2), in an upright brass plate mounted on a small car which slid smoothly on the carefully planed ways of a bedplate. At a second opening, S_1, was placed a plane silvered mirror used as a standard reflector. The back of the upright plate was plane

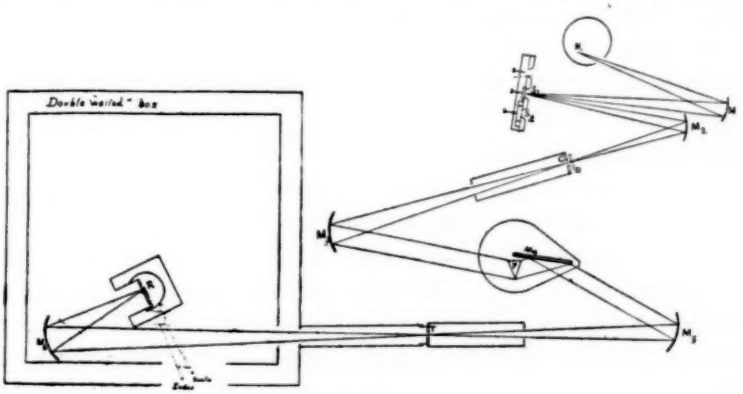

Fig. 2.

so that either the surface whose reflection was to be studied or the standard could be brought successively into the same position by sliding the car along the ways between properly adjusted stops. In the case of plane bright surfaces this adjustment was tested by observing in a telescope provided with cross wires, the position of the image of an incandescent lamp filament reflected first from one and then from the other surface. The adjustment of the more brilliant surfaces was made slightly more exact by the use of three screws which passed through the upright plate and pressed against the silver surface, making it possible to change the angle of the silver until it was in the same plane with the other surface. The adjustment required was in each case so small that but a slight error was introduced by not making the finer adjustment for the duller surfaces after they were clamped in place.

Purification of the Spectrum.—In the preliminary work the energy in the region 18μ to 20μ was found to be unexpectedly great, and it was suspected that this was due, in part at least, to stray energy of shorter wave-lengths. To test this, observations were made on the transparency of quartz, fluorite and rock salt at 20μ where these salts, in plates of the thickness used, were known to be almost entirely opaque. It was found that of the apparent energy at 20μ 70 per cent. was transmitted by quartz, 78 per cent. by fluorite, and 82 per cent. by rock salt.

Of the remaining 18 per cent. not transmitted by rock salt, perhaps 5 to 12 per cent. might be accounted for by diffuse[1] reflection from the surface, and this might also consist of short waves. Therefore, only a remainder of not more than 13 per cent. of the total energy could be considered to be of wave-length 20μ. To get rid of as much as possible of this stray energy, shutters of the three above-mentioned substances were mounted so that either one could be placed in front of the collimator slit at *D* (Fig. 2). Between 4μ and 10μ a plate of quartz 3.5 mm. thick was used, between 10μ and 17μ a plate of fluorite 3 mm. thick, and beyond 17μ a plate of rock salt 4 mm. thick. In the last part of the work the quartz plate was being used for other purposes and a piece of plate glass made a satisfactory substitute.

Method of Making Observations.—When the shutter was in front of the slit, *C*, the energy to which the shutter was transparent produced a deflection of the radiometer suspension and the position of the spot of light on the scale was read. When the shutter was raised the additional deflection was that due to the energy which the shutter formerly cut out and the turning point of the index image on the scale gave a second reading. The shutter was lowered as soon as the extreme swing was reached and the turning point on the backward swing was used. The difference between the second reading and the mean of the first and last is proportional to the energy of the wave-length for which the spectrometer was set and for convenience is called the deflection. The usual order of observing was to take first such a set of readings with the silver surface in the reflecting position. This was followed by three or more sets in which the surface being studied replaced the standard silver surface. In order to make sure that the energy from the Nernst glower had remained constant, a second set of observations was made on the silver surface. If the deflection differed from the first, or if the deflections were small, more observations were made. When the deflections were small the time of a large deflection was determined and the same time allowed between removing or replacing the shutter and reading the scale. Assuming the reflection of silver to be total[2] the ratio of the average deflection with the salt surface in place to that with the standard silver surface in place is called the percentage of reflection. The slit widths were varied from .1 mm. at 4μ corresponding to an interval of .23μ, to 1 mm. corresponding to an interval of .43μ at 20μ. Care was taken to make no changes in the material used for a shutter, or in the slit widths, at a part of the spectrum where the percentage of reflection was changing rapidly.

[1] Pogg. Ann., 138, 174, 1869.

[2] E. Hagen and H. Rubens, Ann. die Phys., II., 73, 1903.

The results are plotted in the accompanying curves in which wave-lengths are chosen as abscissas and percentages of reflection as ordinates. Of the sixteen substances examined ten were ortho-phosphates, two meta-phosphates, and four pyro-phosphates, the typical formulas being respectively R_3PO_4, RPO_3 and $R_4P_2O_7$, where R represents a monovalent base.

Ortho-Phosphates.

The reflection curves for the ortho-phosphates are shown in Figs. 3 and 4. The maxima occur in two distinct parts of the spectrum, one between 9μ and 11μ which for convenience will be referred to as the first region, and the other beyond 16μ or in the second region of maximum reflection. Between these two regions there are no reflection maxima. The curves for the three ortho-phosphates having monovalent bases are put together in Fig. 3. They seem to form a typical set showing clearly that the first point of maximum reflection occurs farther toward the long waves as the atomic weight of the base increases (at. wts. Li = 7, Na = 23, Ag = 108). Of all the salts examined Ag_3PO_4 has the highest and Li_3PO_4 the next highest percentage of reflection. The bases of these two are monovalent and belong to the same chemical group. That the high reflection cannot be attributed to this is shown by the fact that though sodium is also in this group the reflecting power of Na_3PO_4 is one of the lowest. A fourth member of this chemical group, K_3PO_4, was so deliquescent that it was impossible to examine it. All three curves for this monovalent series have two maxima in the second region, each of the two for Ag_3PO_4 being at longer wave-lengths than the corresponding one for Li_3PO_4. But the second for Na_3PO_4 is at a shorter wave-length than the second for Li_3PO_4.

The ortho-phosphates with divalent and trivalent bases are represented by the curves in Fig. 4. They are arranged in the order of the weights of the bases combined with one atomic weight of phosphorus beginning at the bottom with the smallest weight. When the weight of the base is changed these show in general a change in the first region wave-length selectively reflected, similar to that observed in the case of the monovalent series. $Zn_3(PO_4)_2$, and perhaps $Sr_3(PO_4)_2$ with two maxima, are exceptions. There is less regularity in the change of position of the maxima in the second region and the reflection bands are in general more complex. There seems to be no very distinctive difference between the curves for the monovalent and divalent ortho-phosphates. The bases in the latter series—magnesium, calcium, zinc, strontium and lead—belong, with the exception of lead, to the second chemical group. $Sr_3(PO_4)_2$ and $Mg_3(PO_4)_2$ have each two points of maximum reflection in the first region. There

is a rather doubtful indication of a second maximum on the left slope of the first band in $Zn_3(PO_4)_2$ but none with $Ca_3(PO_4)_2$. The general form of the curve for $Pb_3(PO_4)_2$ is very similar to the others, although lead belongs to a different chemical group.

Only two representatives of the ortho-phosphates with trivalent bases could be obtained, $AlPO_4$ and $BiPO_4$. An effort was made to add BPO_4 to the list, but it proved unstable at a certain stage in its preparation. $AlPO_4$ had a very low reflecting power even at the wave-lengths for which the reflection was greatest, although the surface was one of the brightest obtained. There was one rather irregular maximum in the first region, and a probable one beyond 20μ. $BiPO_4$, on the other hand, has high and complex maxima in both regions.

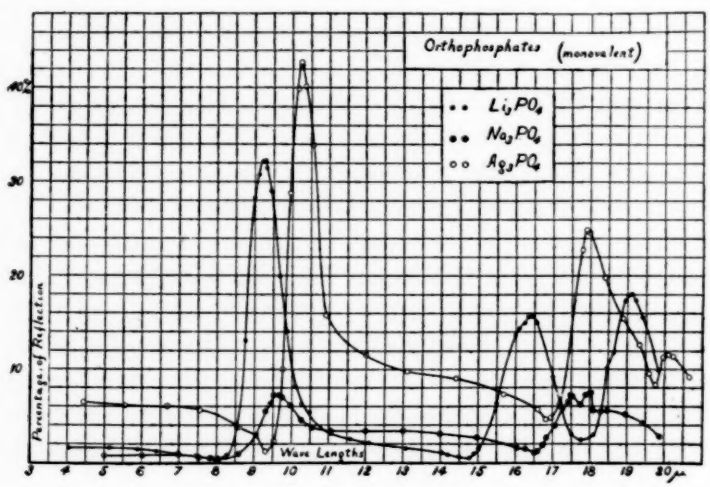

Fig. 3.

It has not been possible with the data obtained to find any distinctive characteristics in the reflection curves which may be ascribed to the chemical group to which the base belongs. Neither have any simple hypotheses suggested themselves which are adequate to interpret the effect of the valence of the base on the complexity of the curves. There seems, however, to be a tendency for the curves to become more complex as the valence of the base increases.

META-PHOSPHATES.

The two meta-phosphates examined, $NaPO_3$ and KPO_3, have monovalent bases. Both curves (Fig. 5) have three reflection maxima between 7μ and 12μ, the middle one being the lowest. $NaPO_3$ was examined to

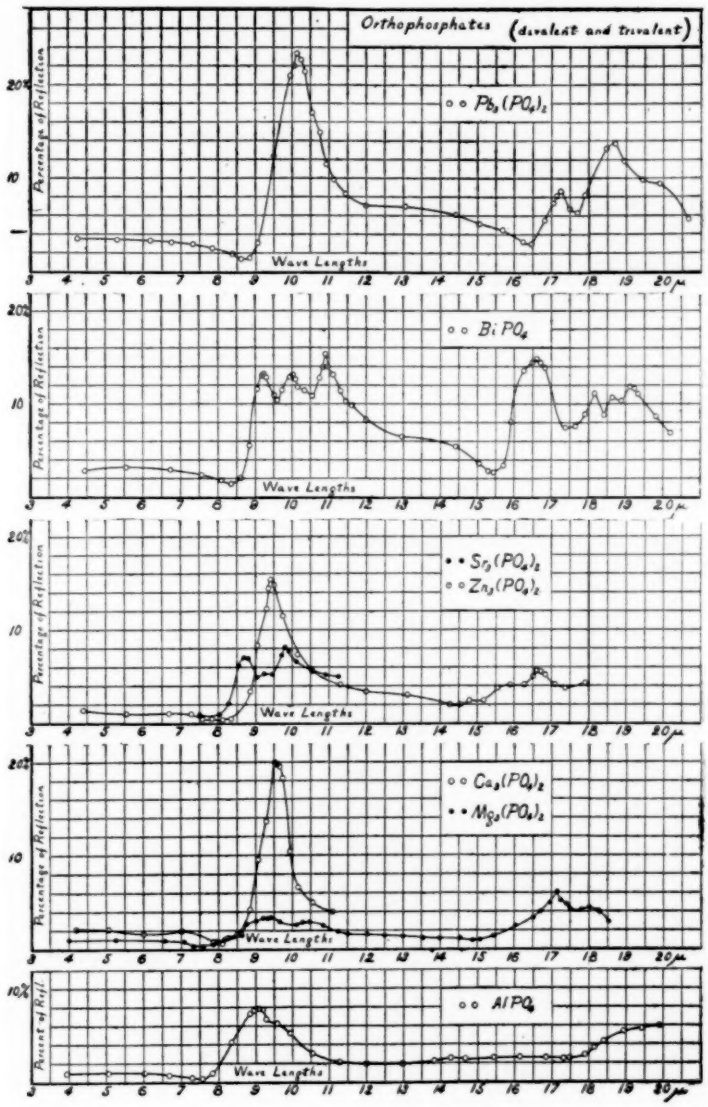

Fig. 4.

20μ and shows a single maximum at 19μ. KPO_3 shows resonance for radiation of greater frequency than does $NaPO_3$ though K has an atomic weight of 39 and Na only 23. Thus an increase in atomic weight of the base is accompanied by a decrease of the wave-length, for which the reflection is a maximum, instead of an increase, as is usually the case. Several different forms of sodium meta-phosphate are known, however, having the formulas $NaPO_3$, $Na_2P_2O_6$, etc., so the sodium meta-phosphate

and the potassium meta-phosphate examined might not have been similar. The $NaPO_3$ was amorphous or glassy, and KPO_3 crystalline. The first maximum for $NaPO_3$ at 7.9μ lies close to that found by Coblentz at 8.0μ.

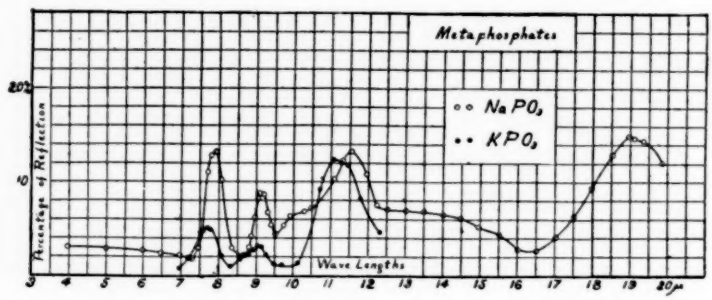

Fig. 5.

PYRO-PHOSPHATES.

Four pyro-phosphates were examined, three with monovalent bases, $Na_4P_2O_7$, $K_4P_2O_7$, $Ag_4P_2O_7$, and one with divalent base, $Pb_2P_2O_7$. A

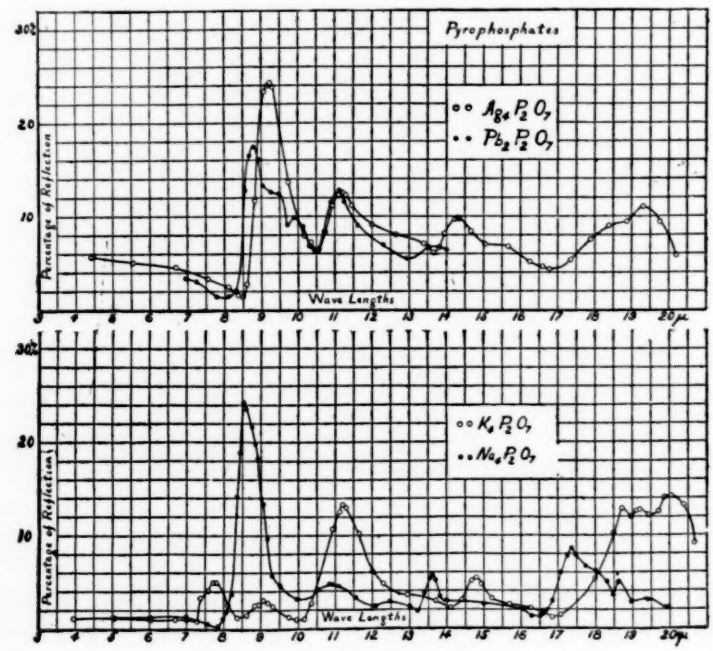

Fig. 6.

distinguishing feature of these curves (Fig. 6) is that they have no region of low or continuously decreasing reflection between 12μ and 15μ as do all the other phosphates examined. Instead, the pyro-phosphates

have in this region one or two points of pronounced selective reflection. The highest points in the $K_4P_2O_7$ curve are at longer waves than the apparently corresponding ones for $Na_4P_2O_7$ with the lighter base, but if all the maxima are taken in regular order without regard to height, the difference is in the opposite sense. There is a somewhat similar correspondence between $Pb_2P_2O_7$ and $Ag_4P_2O_7$; but the two sets cannot be reduced to one depending on the effect of the weights of the bases.

Little more can be said than that these salts with more complex chemical formulas have more free periods of vibration to which they respond than do the simpler molecules. The table is given to assist the reader in locating the more important maxima. The values of the wave-lengths in the last column are taken directly from the curves.

TABLE.

I., Ortho-phosphates; II., Meta-phosphates; III., Pyro-phosphates.

	Chemical Formula of Salt.	Valence of Base.	Atomic Weight of Base.	Weight of Base Combined with One At. Wt. of P.	Wave-lengths of Reflection Maxima.
I.	Li_3PO_4	1	7	21	9.25, 16.4–19.1
	$AlPO_4$	3	27	27	9.1, (20)
	$Mg_3(PO_4)_2$	2	24	36	9.4, 10.5,17.1
	$Ca_3(PO_4)_2$	2	40	60	9.5,
	Na_3PO_4	1	23	69	9.6, 17.5–18.0
	$Zn_3(PO_4)_2$	2	65	98	9.4, 16.6
	$Sr_3(PO_4)_2$	2	87	130	8.7–9.8
	Bi_3PO_4	3	207	207	9.2–10.0, 16.6–18.15 10.9, 18.60–19.15
	$Pb_3(PO_4)_2$	2	206	309	10.15, 17.25–18.7
	Ag_3PO_4	1	108	324	10.25, 17.9–20.1
II.	$NaPO_3$	1	23	23	7.9–9.15–11.6, 19.0
	KPO_3	1	39	39	7.7–9.1–11.1
III.	$Na_4P_2O_7$	1	23	46	8.5–10.9, 12.5–13.6, 17.4–18.7
	$K_4P_2O_7$	1	39	78	7.75–9.05, 11.2–14.8,
	$Pb_4P_2'_7$				18.7–19.15, 20.0
	$Pb_2P_2O_7$	2	206	206	8.–89.5,9.9–11.1, 13.5
	$Ag_4P_2O_7$	1	108	216	9.2–11.2, 14.3–19.3

Fig. 7 shows the position of the most prominent reflection maxima for the ortho-phosphates plotted with wave-lengths as abscissas and as ordinates the weights of the bases united with one atomic weight of phosphorus. To show the magnitude of the deviations from exact proportionality between the wave-lengths and weights of the bases, a straight line has been drawn through the Li_3PO_4 and Ag_3PO_4 maxima in the first

region. It is seen from this figure that the deviations do not bear any constant relation to the valence of the base. In the second region two lines have been drawn which include between them all except one of the principal maxima. This region of selective reflection is nearly 3μ broad

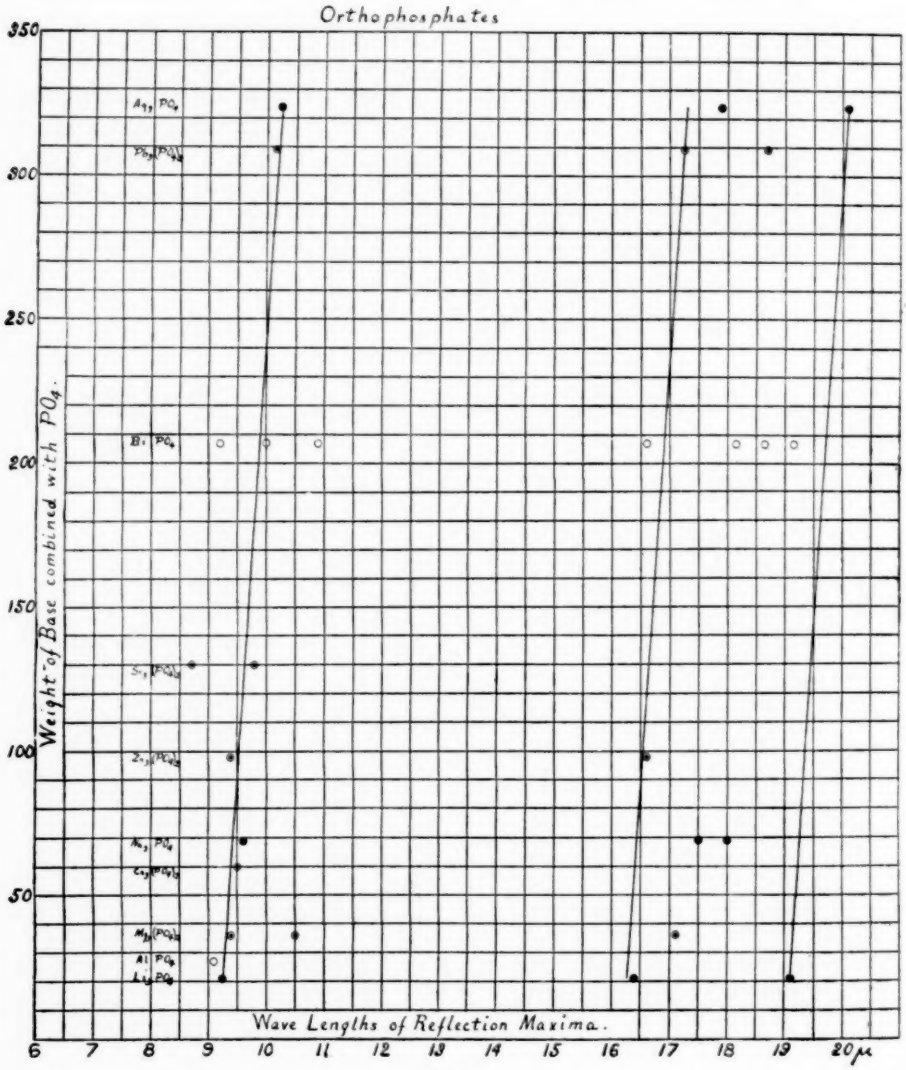

Fig. 7.

and shows a general shift to the long waves with increasing weight of base, though no correspondence between individual maxima can be traced.

It has been shown that[1] a change in the atomic weight of the element

[1] Astrophysical Journal, 26, p. 240, 1907.

combined with oxygen in the acid radical seems to have a greater effect on the position of the reflection band than an equal change in the atomic weight of the base. A comparison of the curves for phosphates with those for sulphates[1] shows that in all cases the first region bands for the ortho-phosphates are at longer wave-lengths, on an average fully .7μ, than those for the corresponding sulphates. This difference cannot be attributed to a difference only in the atomic weights of phosphorus and sulphur for the two have approximately the same weights, that for sulphur being slightly larger (S = 32.0, P = 31.0). Neither does it seem that a difference in the weights of the bases can account for more than a small part of the difference in wave-lengths selectively reflected. This is certainly true if we may for example assume that K_2 and K_3 in K_2SO_4 and K_3PO_4 act similarly to bases of atomic weights 2×39 and 3×39 respectively. If we should assume that oxygen is the determining element and that the position of the reflection maxima is due to the loading of the oxygen atom with atoms in combination with it, it might be inferred that not only would the precise position be affected by the weight of the base and the acid forming element, but also that the strength of the bonds and the arrangements of the atoms in the molecule would have some influence. Phosphorus has a much stronger affinity for oxygen than has sulphur, for the oxides of phosphorus are decomposed with greater difficulty. What relation this bears to the selective reflection of the solid salts it is impossible to determine with present data.

Merritt[2] and Königsburger[3] both found that between .1μ and 5.5μ the absorption in doubly refracting media depended upon the plane of polarization of the incident energy. Later it was observed that the reflection maxima of calcite and aragonite[4] in the 11μ region differed by .24μ though both calcite and aragonite had the same chemical formula, $CaCO_3$. There were also decided differences in the heights of the reflection maxima, which could not be attributed to a difference in polish. This showed conclusively that the crystal form as well as the chemical composition must be taken into account even when dealing with radiations of wave-lengths over 10μ. More recently the dependence of the selective reflection on both the crystal form and the orientation of the section examined has been very carefully studied by Nyswander[5] in the case of calcite and aragonite using polarized light.

In order to obtain a complete analysis of the dependence of free reso-

[1] Investigations of Infra-red Spectra, Parts IV. and VI.

[2] PHYS. REV., 2, 424, 1895.

[3] Ann. der Phys., 61, 687, 1897.

[4] Astrophysical Journal, 11., 225, 1907.

[5] PHYS. REV., 28, 4, p. 291, 1909.

nance periods upon the chemical composition of a salt it will be necessary to examine the substance in crystal form and with polarized light. It is, as has already been stated, impossible to find suitable crystal sections of an extended series of salts which have the desired variations in chemical composition. While pressed surfaces cannot give the absolute values of reflection, the minute crystalline structures when present must have all possible orientations and therefore all the free resonance periods of sufficient strength must appear in the resulting curves. A comparison of the relative heights of the reflection maxima observed with pressed surfaces is certainly more trustworthy than such a comparison when crystal sections cut at random are used. For example, the almost complete disappearance of the second region maximum in the witherite examined by Morse[1] is undoubtedly due to the chance orientation of the crystal section. The use of pressed surfaces makes possible the examination of a great number of large and complicated series of salts like the phosphates here described. And the data thus obtained promise eventually to be of much value in selecting the crystal sections best suited to a more complete investigation of the problem.

The main results here presented may be summarized as follows:

1. A surface suitable for the qualitative study of selective reflection in the infra-red spectrum may be produced on a substance which is available only in the form of fine powder, if this powder is subjected to great pressure.

2. The method of making the pressed surfaces described has made it possible to compare the reflection in the infra-red spectrum of extended series of salts, such as phosphates, chromates or chlorates in which a common acid forming element is combined with different weights of oxygen. Data on the selective reflection of phosphates are here given.

3. A comparison of Figs. 3 and 4 for ortho-phosphates with Fig. 5 for meta-phosphates and Fig. 6 for pyro-phosphates shows that each group has a more or less characteristic selective reflection which easily distinguishes it from the other groups of phosphates as well as from salts of other acids, carbonates, nitrates, and sulphates.

4. The data on phosphates alone are an insufficient basis for the formulation of any exact relation between the valence of the base, or the chemical group to which it belongs, and the selective reflection characteristic of the salts of a given acid radical. But in general an increase in the weight of the base combined with the given acid radical containing phosphorus causes the reflection maxima to be moved toward the longer waves, as has been found with salts of other acids.

[1] Astrophysical Journal, 26, p. 240, 1907.

5. A comparison of sulphates and phosphates shows that phosphorus has a greater effect on the free resonance periods than sulphur for some reason not connected with the relative atomic weights since the reflection maxima occur for longer waves in the phosphates, although phosphorus and sulphur for the rough purposes in hand have practically the same atomic weight.

In conclusion the writer wishes to thank Mr. B. L. Murray, of Merck and Company, for aid in the selection of the phosphates used. She also wishes to thank Dr. L. B. Morse for his interest and assistance throughout the work. And she especially wishes to acknowledge her great indebtedness to Dr. E. F. Nichols who suggested the investigation, and under whose direction is was carried out.

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